BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1936.

General, Physical, and Inorganic Chemistry.

Atomic hydrogen and the disappearance of hydrogen in discharge tubes. R. Delaplace (Compt. rend., 1936, **202**, 1986—1987).—If traces of H_2O vapour and Hg are excluded from the discharge, no fall in pressure occurs and no CO and CH_4 are formed. In absence of H_2O vapour the formation of at. H is restricted. Heating the glass liberates traces of CO_2, CO, and H_2. H. J. E.

Intensities in the principal series of lithium. S. Weintroub (Proc. Physical Soc., 1936, **48**, 535—548).—The effect of using orthogonal wave functions in the calculation of the optical terms and oscillator strengths (*f* nos.) of the first three lines of the principal series of Li has been investigated. Good agreement with observed vals. is obtained for the optical terms; the agreement for the *f* nos. is not so good, but is better than that obtained using non-orthogonal wave functions. W. R. A.

Spectra Be III and Be IV. H. A. Robinson (Physical Rev., 1936 [ii], **50**, 99).—New determinations of the λλ of the $1s^{2\,1}S_0 - 1s\,.\,np\,^1P_1$ series of Be III and the $1s^2S - np^2P$ series of Be IV are recorded. A. J. M.

Absorption coefficients of the 4774, 5770, and 6290 A. oxygen bands. L. Herman and (Mme.) R. Herman-Montagne (Compt. rend., 1936, **202**, 2064—2066).—Data are recorded. The absorption ∝ the square of the pressure (4—12 kg. per sq. cm.). H. J. E.

Influence of carbon monoxide, adsorbed by a platinum electrode, on the current–potential relations of the electrical discharge in oxygen. V. Sihvonen (Z. Elektrochem., 1936, **42**, 538—544).—In streaming O_2 at low pressure CO is produced at a C anode and is oxidised to CO_2 by O_2 adsorbed by a Pt cathode. When C is the cathode, CO is strongly adsorbed by the Pt anode and prevents emission of ions until removed by the streaming O_2, when the current momentarily passes. E. S. H.

Stark effect in neon. N. Ryde (Z. Physik, 1936, **100**, 771—773).—Polemical, against Steubing and Kindler (this vol., 653). A. B. D. C.

[Stark effect in neon.] W. Steubing and H. Kindler (Z. Physik, 1936, **100**, 773).—A reply to Ryde (see above). A. B. D. C.

Transparency of sodium and potassium films in the Schumann region. W. H. Watson and D. G. Hurst (Nature, 1936, **138**, 124).—A Na film on fluorite is an ideal filter to remove all visible and ultra-violet light of $\lambda > 2100$ A., and to pass the entire Schumann region. The results for Na and K do not support the existing theory of the optical properties of metals. L. S. T.

Isotope shift in the resonance line of magnesium. D. A. Jackson and H. Kuhn (Proc. Roy. Soc., 1936, **A**, **154**, 679—683).—The singlet resonance line 2852 A. of Mg is shown by the at. beam method to possess two components at a separation of 0·033 $cm.^{-1}$, the component of longer λ being much stronger than the other. The splitting of the line is ascribed to an isotope shift, the stronger line being due to the abundant isotope 24 and one of the other two, and the weaker line to the third isotope. L. L. B.

Band spectrum of sulphur. A. Christy (Physical Rev., 1935, [ii], **47**, 251).—A reply to criticism (this vol., 397). L. S. T.

Optical L spectra of chlorine, Cl VIII, Cl IX, Cl X, and Cl XI. B. Edlén (Z. Physik, 1936, **100**, 726—733). A. B. D. C.

Nuclear spin and magnetic moment of potassium (41). J. H. Manley (Physical Rev., 1936, [ii], **49**, 921—924; cf. Fox, this vol., 1).—The spin of the ^{41}K nucleus and the hyperfine structure separation of the $^2S_{\frac{1}{2}}$ normal state were measured by the method of zero moments, the high resolution for separating the two isotopes being obtained by passing a beam of neutral K atoms through a weak inhomogeneous magnetic field 153 cm. long. The spin was 3/2, and the hyperfine structure separation and magnetic moments $0{\cdot}554 \pm 0{\cdot}2\%$ of those of ^{39}K, the vals. of which give for ^{41}K 0·22 nuclear Bohr magneton and $0{\cdot}00853 \pm 0{\cdot}0001$ $cm.^{-1}$ for magnetic moment and separation, respectively. The abundance ratio $^{39}K/^{41}K$ is $13{\cdot}4 \pm 0{\cdot}5$. N. M. B.

Narrow continuous band of potassium in the extreme red. T. Okuda (Nature, 1936, **138**, 168).—A broadening of the resonance lines in the extreme red absorption spectrum of K vapour in H_2, and the appearance, at higher temp., of a narrow, continuous band at approx. 7220 A. has been observed. L. S. T.

Use of the reflexion echelon for interferometric wave-length comparisons extending into the Schumann region. D. L. MacAdam (Physical Rev., 1936, [ii], **50**, 185).—Measurements of eight $\lambda\lambda < 2100$ A. for Cu II agree to $< 0{\cdot}004$ A. with calc. vals. Difficulties of the method are discussed. N. M. B.

Emission spectrum of diatomic arsenic. G. M. Almy and G. D. Kinzer (Physical Rev., 1935, [ii], **47**, 199).—The mol. spectrum of As in emission consists of an extensive group of bands between 2250 and 3750 A. and a weak group near 4200 A. L. S. T.

Structure of bromine III. K. R. Rao (Nature, 1936, **138**, 168).—An extension of previous work (A., 1935, 423). L. S. T.

Hyperfine structure of the cadmium resonance line. A. G. Shenstone (Physical Rev., 1935, [ii], 47, 317). L. S. T.

Fluorescence spectra of antimony vapour excited by cadmium, zinc, and magnesium sparks. R. Siksna (Acta phys. polon., 1933, **2**, 253—265; Chem. Zentr., 1935, ii, 3062).—Data for the line and band fluorescence are given. H. J. E.

Fluctuation bands of the vapour of diatomic tellurium. M. Désirant and A. Minne (Bull. Acad. roy. Belg., 1936, [v], **22**, 646—658).—A series of wide and symmetrical bands showing fluctuations in intensity have been observed in the spectrum of the vapour of Te_2. The bands are composed of numerous fine bands degraded towards the red. Two systems may be recognised, one extending from the last bands of the principal system to 6000 A., the other from 6000 A. into the red. The heat of dissociation for the normal state of Te_2 is calc. to be 2·3 volts. A. J. M.

First spark spectrum of cæsium as excited by electron impact. R. R. Sullivan (Physical Rev., 1936, [ii], 49, 912—916).—An apparatus for the study of the controlled excitation of spectra of volatile metals is described. Certain aspects of the optical excitation functions for several Cs II lines are given. Onset potentials are compared with those predicted by existing energy level schemes, and possible transitions are suggested for the unclassified lines λλ 4264·7 and 4763·6. N. M. B.

Resonance radiation of mercury 2536·7 A. line, avoiding Doppler broadening. S. Yen (Helv. phys. Acta, 1935, 8, 225—246; Chem. Zentr., 1935, ii, 2782).—The Doppler broadening is avoided by exciting the resonance line in a beam of Hg at. rays. Zeeman resolution of the line is observable with very low magnetic fields, revealing a new magnetic effect. J. S. A.

Paschen–Back effect of hyperfine structure. III. Separation of ^{199}Hg. J. B. Green (Physical Rev., 1936, [ii], 50, 126—128; cf. A., 1935, 137).—The magnetic components due to ^{199}Hg have been separated. The lines studied were λλ 3125, 5461, 4358, and 4047. An almost complete Paschen–Back effect is observed, each ordinary Zeeman component being accompanied by two satellites due to the nuclear spin $i=\frac{1}{2}$. Results agree closely with theory. N. M. B.

Afterglow in electrically excited mercury vapour. K. Narkiewicz-Jodko (Acta phys. polon., 1933, 2, 311—333; Chem. Zentr., 1935, ii, 3064).—Measurements at 100—300°/2·6—87 mm. are recorded. The min. pressure for the afterglow was 2 mm. The effective diameter of excited Hg was 6×10^{-8} cm., assuming a life of 10^{-7} sec. H. J. E.

Distribution of atomic nuclear spins. S. Tolansky (Nature, 1936, **137**, 1071; A., 1935, 676).—Diagrams showing the distribution of nuclear spins in atoms of odd at. wt. are given. The preponderance of spin of val. $\frac{1}{2}$ in the case of nuclei with an odd nuclear neutron indicates that neutron spin and orbital moments tend to oppose each other. L. S. T.

Electrical discharge between rotating copper electrodes. A. Kotecki (Acta phys. polon., 1934, 3, 105—114; Chem. Zentr., 1935, ii, 3209).—The voltage drop across a 10-mm. arc in air at atm. pressure does not vary with the speed of rotation of the electrodes (Cu or Al). H. J. E.

Second sheath near the [oxide-coated] cathode of an arc discharge [in rare gases]. N. Warmoltz (Nature, 1936, **138**, 36). L. S. T.

Ultra-violet stellar spectra with aluminium-coated reflectors. IV. Spectrum of α Boötis. R. W. Shaw (Astrophys. J., 1936, **83**, 225—237).—Lines between 3150 and 3950 A. are tabulated. Al, Cr, Cu, Fe, Ni, Na, Ti, and V, and the NH mol. spectrum have been identified. L. S. T.

Effect of oxygen on the auroral afterglow. J. Kaplan (Nature, 1936, **138**, 35). L. S. T.

Absorption-line intensities in *B*-type stars. E. G. Williams (Astrophys. J., 1936, **83**, 279—304). L. S. T.

Connexion between emission intensity and violet displacement of the absorption lines in the spectrum of P. Cygni. T. Araki and M. Kurihara (Proc. Imp. Acad. Tokyo, 1936, **12**, 125—127). A. J. M.

***X*-Ray wave-length scales.** A. E. Ruark (Physical Rev., 1935, [ii], **47**, 316; cf. A., 1934, 833).—When $4·806\pm0·003\times10^{-10}$ e.s.u. is used for e and $1·7579\times10^{7}$ e.m.u./g. for e/m, the discrepancy between measured photo-electron energies and those calc. from *X*-ray λλ is explained. L. S. T.

Absorption of *X*-rays of wave-length 50 to 150 A. by elements of low atomic number. T. R. Cuykendall (Physical Rev., 1936, [ii], **50**, 105—109).—Mass absorption coeffs. accurate to 2% were determined for C, Na, Al, S, K, Ni, and Cu for the range 50—209 A. Vals. of the electronic scattering coeff. by the Klein–Nishina formula are in good agreement with experiment for C in the range 40—100 X. The photo-electric absorption in Cu is $\propto \lambda^{2·83}$. N. M. B.

Absorption of ultra-short *X*-rays by elements of high atomic number. M. T. Jones (Physical Rev., 1936, [ii], 50, 110—114; cf. preceding abstract).—Mass absorption coeffs. accurate to 0·8% were measured for Pb, Ta, Sn, Ag, Mo, and Nb for the range 30—185 A. Photo-electric absorption is calc. and discussed in relation to at. no. and the Klein–Nishina formula. N. M. B.

Structure of the extremely soft *X*-ray absorption of solids. H. M. O'Bryan (Physical Rev., 1936, [ii], 49, 944).—The absorption of Li and Mg on celluloid and of Li and Na halides in the range 170—500 A. shows, for Li, an additional band at 196 and a faint edge at 225 A.; LiCl gives very sharp bands

at 204 and 192 A., the other Li halides give similar bands, but the Na halides only one prominent band at 372 A. Mg halides show a band near 235 A. Mg gives a stronger edge at 237 than at 250 A. The bands for the halides are due to the alkali ion of the crystal. There must be two sets of lattice levels. Results are in poor agreement with calculations.
N. M. B.

Shape of the Compton lines. A. Sommerfeld (Physical Rev., 1936, [ii], **50**, 38—40).—The continuous Compton band observed for bound electrons must have a definite limit on the short-wave side. Beyond this limit, and up to the unmodified Rayleigh line, there should be a no. of discrete lines, which may be termed Raman lines. There is no discontinuity in the intensity. The experimental conditions for observing these lines are discussed and it is suggested that lines observed by Ray in the spectrum of *X*-rays which have passed through thin films (A., 1930, 833) might thus be explained.
A. J. M.

Correlation between scattering and recoil in the Compton effect. J. C. Jacobsen (Nature, 1936, **138**, 25).—Experiments with γ-rays from Ra-Th confirm the usual theory of the Compton effect (cf. this vol., 265). L. S. T.

Relative and absolute values of atomic levels. A. E. Sandström (Phil. Mag., 1936, [vii], **22**, 171—180).—A discussion of data obtained from *X*-ray absorption spectra and from the magnetic deflexion of secondary electrons. H. J. E.

Natural width of the $K\alpha$ lines. H. Margenau (Physical Rev., 1935, [ii], **47**, 89—90). L. S. T.

K Radiation of boron. J. Serpe (Compt. rend., 1936, **202**, 1979—1981).—The *K* radiation of powdered B is a single continuous band. The effect of temp. on its structure is discussed. H. J. E.

K Radiation of crystallised boron. A. Hautot (Compt. rend., 1936, **202**, 2138—2140).—The increase of conductivity and the variation in the *K* radiation bands with rise of temp. for cryst. B prepared by reducing BCl_3 with H_2 in a condensed high-frequency spark are explained on the supposition that the valency electrons are held in the crystal lattice at low temp. (600°), and are liberated at high temp. (1530°). C. R. H.

$K\alpha$ Satellite lines. L. G. Parratt (Physical Rev., 1936, [ii], **50**, 1—15).—The $K\alpha_{3,4}$ group of *X*-ray satellite lines has been recorded for the elements from S (at. no. 16) to Ge (32). For elements of at. no. between 16 and 28 there are five components of the satellite lines, and for those between 29 and 32 there are four. The widths, indices of asymmetry, and overlapping factors of the $K\alpha_{1,2}$ lines were also determined. The effect of chemical linking, determined by using targets of various Ca compounds, was negligible. A. J. M.

$L\alpha$ Satellites for the elements 72, 73, 75, 83, 90, and 92. (Mlle.) Y. Cauchois (Compt. rend., 1936, **202**, 2068—2069; cf. this vol., 3).—Data are summarised and discussed. H. J. E.

Formation of a potassium film on silver. J. J. Brady (Physical Rev., 1935, [ii], **47**, 197).—The photo-electric properties of K films deposited on a freshly evaporated Ag surface have been investigated with special reference to the saturation of the photo-current. L. S. T.

Use of the image potential for the surface photo-electric effect. R. D. Myers (Physical Rev., 1936, [ii], **49**, 938—939).—The calc. surface photo-electric effect, taking account of the image force between electron and metal, shows an increased no. of slow electrons and a somewhat steeper max. of the effect as a function of the illuminating frequency.
N. M. B.

Photo-electric effect of the deuteron. G. Breit and E. U. Condon (Physical Rev., 1936, [ii], **49**, 904—911).—Theoretical cross-sections for the dissociation of the deuteron by absorption of γ-rays (the Chadwick–Goldhaber effect) are calc., and curves of cross-section as a function of energy for various assumed widths are given and discussed. N. M. B.

Thermionic emission from platinum in bromine and chlorine vapour. S. Kalandyk (Acta phys. polon., 1934, **3**, 165—178; Chem. Zentr., 1935, ii, 3209—3210).—The negative emission from Pt is increased by the presence of Br and occurs at a relatively low temp. (160° for 0·235 mm. Br pressure). The effect increases with the Br pressure. It is attributed to a chemical reaction. The + emission is unchanged. At very high temp. the normal emission from Pt is observed. Similar results were obtained for Cl_2 and I. H. J. E.

Ionisation of gases by collisions of their own accelerated atoms. R. N. Varney (Physical Rev., 1936, [ii], **50**, 159—161).—Neutral atom beams of rare gases of energies 20—400 volts were produced by accelerating ionised atoms and then neutralising the charges. The min. energies needed by these neutral atoms to ionise gas atoms by collision were determined. Ne, A, Kr, and Xe ionised their own gases at energies about three times the actual ionisation potentials. N. M. B.

Total ionisation of nitrogen by electron collisions. (Miss) G. A. Anslow and (Miss) M. de B. Watson (Physical Rev., 1936, [ii], **50**, 162—169).—The total ionisation by beams of electrons of homogeneous velocity and energies $\ngtr$ 1500 volts increases rapidly up to 75 volts, then less rapidly but linearly to 375 volts, for which there is a break in the ionisation curve, indicating the onset of *K* electron ionisation; the ionisation again increases rapidly near 750 volts and less rapidly but linearly after 1200 volts. The mean effective ranges and electron energies nearly obey the relation $R_e=0{\cdot}07+1{\cdot}88\times10^{-6}V^2$ cm. at 1 mm. pressure. The average total ionisation per cm. of absorbing gas layer shows a max. above 100 volts in the primary ionisation region and a second max. at 750 volts, twice the ionisation potential of the *K* electrons of N, these characteristics being similar to those for air
N. M. B.

Secondary electron emission from a hot nickel target due to bombardment by hydrogen ions. (Miss) M. Healea and E. L. Chaffee (Physical Rev., 1936 [ii], **49**, 925—930).—Consistent vals. were obtained after keeping the target hot for 6 weeks. The no. of electrons emitted from the target per positive ion varied from 0·046 at 303 e.v. to 0·223 at 1539 e.v. ion energy. N. M. B.

(A) **Inelastic scattering of electrons from solids.** E. Rudberg. (B) **Theory of inelastic scattering of electrons from solids.** E. Rudberg and J. C. Slater (Physical Rev., 1936, [ii], **50**, 138—150, 150—158).—(A) The energy distribution of electrons scattered inelastically from Cu, Ag, and Au surfaces deposited in vac. was investigated for the energy range 50—400 volts. For certain vals. of the energy loss suffered by the scattered electron the curves show max. characteristic of the material and independent of the primary voltage. Each metal has two max. below 10 volts, and these appear to correspond roughly with regions of high optical absorption. The penetration depth of the scattered electron, estimated from energy distribution measurements on films of Ca, CaO, Ba, and BaO of known thickness deposited on Ag, shows that inelastic scattering is determined by the first few at. layers near the surface. The Ca and Ba deposits show a high rate of oxidation, even at $< 10^{-7}$ mm. pressure. The distribution curves for the oxides differ entirely from those for the metal.

(B) Mathematical. A detailed calculation is given for Cu. The distribution curve and its two max. are in good agreement with experiment. N. M. B.

Anomalies in the charging of gas molecules by slow ions. F. Wolf (Naturwiss., 1936, **24**, 447—448).—An earlier method (this vol., 539) has been improved, and the form of the charge transference cross-section against ionic velocity studied for $H_2^+ \rightarrow N_2$, $H^+ \rightarrow A$, and $H^+ \rightarrow H_2$ for low ionic velocities. There is a more or less definite secondary max. or min. in the curves at low velocities. A. J. M.

Production of radiation and ionisation from helium atoms by potassium positive ions. (Miss) A. C. Davies (Proc. Roy. Soc., 1936, A, **155**, 123—141).—The excitation and ionisation of neutral He atoms by a beam of K^+ ions of controlled energy has been investigated. The beginning of measurable ionisation plus radiation effects occurs at about 450 volts. The no. of electrons produced per K ion per cm. of path at a 1 mm. pressure by 750-volt ions is estimated as $8{\cdot}7 \times 10^{-3}$, and by 3000-volt ions as $2{\cdot}3 \times 10^{-1}$. Possible causes of the discrepancies in results of previous investigators are discussed. L. L. B.

Preparation and investigation of a new alkali ion source. J. Koch (Z. Physik, 1936, **100**, 669—684).—An alkali chloride mixed with degassed W powder is a very pure source of Cs, Rb, and K ions. A. B. D. C.

Incidence of positive cæsium ions on a degassed tungsten surface. J. Koch (Z. Physik, 1936, **100**, 685—701).—Cs ions incident on a W surface are largely reflected, and the saturation Cs layer is $< 0{\cdot}1$ monat. A. B. D. C.

New process of negative ion formation. F. L. Arnot (Nature, 1936, **138**, 162).—The majority of negative ions formed by the passage of a stream of electrons through Hg vapour, H_2, N_2, O_2, and CO_2 do not arise by the attachment of an electron to an atom. They are formed from positive ions which extract two electrons from any negatively charged electrode, including the filament, to which they are driven. Occasionally the positive ion is dissociated by its collision with the surface and the negative ion then formed is one of the products of dissociation; *e.g.*, the negative ions detected in CO_2 are CO_2^-, CO^-, O_2^-, O^-, and C^-. In O_2, both O_2^- and O^- are found, but Hg vapour, H_2, and N_2 give only the at. negative ion. The probability of conversion of positive into negative ions on a Ni surface in each gas increases as the energy of the positive ion is increased, and data for the conversion of a 180-volt positive ion are recorded. L. S. T.

Fundamental at. wts. Ratio of silver nitrate to silver chloride. O. Hönigschmid and R. Schlee (Angew. Chem., 1936, **49**, 464—466).—The mean of eight determinations yields a val. of 1·185241 for the ratio $AgNO_3 : AgCl$. Combining with the vals. 1·57479 and 4·042592 for the ratios $AgNO_3 : Ag$ and $AgCl : Cl$, respectively, the at. wts. of Ag, Cl, and N are 107·8812, 35·4562, and 14·0088, respectively. J. W. S.

Calculation of at. wts. from nuclear reaction energies. H. A. Wilson (Proc. Roy. Soc., 1936, A, **154**, 560—563; cf. A., 1935, 1443).—It is shown that at. wts. with $^{16}O=16$ can be calc. from nuclear reaction energies without making use of at. wts. determined by other methods. Vals. obtained for 18 light elements in this way are in agreement with those of Bethe and of Oliphant, Kempton, and Rutherford from mass spectrograph results (cf. A., 1935, 910). L. L. B.

Masses of ^{8}Be, ^{9}Be, and ^{11}B as determined from transmutation data. H. R. Crane and C. C. Lauritsen (Physical Rev., 1935, [ii], **47**, 420).—Vals. deduced are ^{8}Be 8·0059, ^{11}B 11·0095 or 11·0093, ^{9}Be 9·0125 (approx. 2 α-particles + 1 neutron). L. S. T.

Differences in the isotopic composition of atmospheric and aqueous oxygen and the electrolytic separation factor of oxygen isotopes. N. Morita and T. Titani (Bull. Chem. Soc. Japan, 1936, **11**, 414—418).—The *d* of light H_2O prepared by combination of D_2-free H_2 and atm. O_2 indicates that atm. O_2 is 0·0007% heavier than O_2 from H_2O, and that the electrolytic separation factor for O_2 isotopes is $1{\cdot}01 \pm 0{\cdot}01$. C. R. H.

Influence of density differences between atmospheric and aqueous oxygen on data for oxygen and hydrogen isotopes. N. Morita and T. Titani (Bull. Chem. Soc. Japan, 1936, **11**, 419—424).—Contemporary vals. for the ratio D : H and for the electrolytic separation factor for O isotopes are compared and discussed. C. R. H.

Isotopes in induced radioactivity. T. R. Wilkins and L. S. Shnidman (Physical Rev., 1935, [ii], **47**, 251).—The final stable products of nuclear transformations resulting from α-ray bombardment, viz., $^{30}_{14}$Si, $^{13}_{6}$C, $^{27}_{13}$Al, etc., are all isotopes of rarest occurrence according to mass spectrum data. In transformations from neutron bombardment the resulting stable atoms such as $^{16}_{8}O$, $^{24}_{12}Mg$, $^{32}_{16}S$, etc. are the most frequently occurring isotopes. Transformations occurring in nature thus appear to be more frequently of the neutron type. L. S. T.

Isotopic constitution of iron and nickel. A. J. DEMPSTER (Physical Rev., 1936, [ii], **50**, 98).—The mass spectrum of Fe obtained by sparking between pure electrolytic Fe electrodes indicates the existence of isotopes of Fe of mass 54, 56, 57, and 58, the last being the weakest. The mass spectrum of Ni obtained by fractionating $Ni(CO)_4$ showed the presence of isotopes of mass 58, 60, 61, 62, and 64. A. J. M.

Mass spectrograph analysis of bromine. J. P. BLEWETT (Physical Rev., 1936, **49**, 900—903).—Attempts to observe a third isotope to explain the three periods of artificial radioactivity induced by slow neutrons show that an isotope 77 or 83 cannot be present to more than 1 in 3000. The abundance ratio 81/79 was $0{\cdot}975 \pm 0{\cdot}025$, giving the at. wt. of Br $79{\cdot}92 \pm 0{\cdot}02$ on Aston's scale or $79{\cdot}90 \pm 0{\cdot}02$ on the at. wt. scale. The processes of formation of positive and negative Br ions by slow electrons were studied, giving heat of dissociation of Br_2 $1{\cdot}9 \pm 0{\cdot}5$ volts, and electron affinity of Br $3{\cdot}8 \pm 0{\cdot}2$ volts. N. M. B.

Isotopic constitution of barium and cerium. A. J. DEMPSTER (Physical Rev., 1936, [ii], **49**, 947; cf. Blewett, this vol., 772).—Mass spectra photographs of Ba ions formed in a high-frequency spark between Ba electrodes show very faint isotopes at 130 and 132; Ce gives similar results at 136 and 138. On a neutron–proton plot of the isotopes ^{130}Ba and ^{136}Ce fall on the straight line indicating the lower mass limit for nuclear stability. N. M. B.

Isotopic constitution of strontium and tellurium. A. J. DEMPSTER (Physical Rev., 1936, [ii], **50**, 186).—^{84}Sr is confirmed (cf. Blewett, this vol., 772). Mass spectra of the charged atoms from a spark between Te and Pd electrodes show a new faint ^{120}Te, but no trace of ^{127}Te indicated by Bainbridge (cf. A., 1933, 1099). N. M. B.

Mass equivalent of the energy in radioactive transformations. A. J. DEMPSTER (Nature, 1936, **138**, 201).—A spark between electrodes of Pb and Pd or Pt–Rh forms doubly-charged Pb ions which give close doublets in the mass spectrograph with the singly-charged Rh and Pd ions at 102, 103, and 104. The at. masses deduced for the Pb isotopes are $206{\cdot}00 \pm 0{\cdot}01$ and $208{\cdot}00 \pm 0{\cdot}01$. These vals. agree with those obtained for U-Pb and Th-Pb from the radioactive transformations of U and Th, provided that an allowance is made for the mass equivs. of the energy emitted in these processes. L. S. T.

Isotopic constitution of lead from hyperfine structure. J. L. ROSE and R. K. STRANATHAN (Physical Rev., 1936, [ii], **49**, 916—920; cf. A., 1935, 272).—The % relative abundances of the Pb isotopes, determined from intensity measurements of the hyperfine structure components of the spark line λ 5372, were 51·5, 26·3, 21·4, and 0·8 for isotopes 208, 206, 207, and 204, respectively. For integral masses of the isotopes the mean mass no. is $207{\cdot}22_8$, giving 207·20 on the at. wt. scale, assuming a packing factor of +1. N. M. B.

Atomic masses of uranium and thorium. A. J. DEMPSTER (Nature, 1936, **138**, 120).—Doublets obtained in the mass spectrograph with $Th^{\cdot\cdot}$ and ^{116}Sn, and $U^{\cdot\cdot}$ and ^{119}Sn give 232·070 and 238·088 (O=16·000) for the at. masses of Th and U, respectively. Doubly-charged ions of ^{235}U, mass $235{\cdot}084 \pm 0{\cdot}01$, also appeared. Reduced to the chemical scale, the at. wts. become 232·024 for Th and 238·028 for the mean of the two U isotopes, compared with the accepted vals. of 232·12 and 238·14, respectively. Electrodes prepared from heated $UO_2(NO_3)_2$ and Na uranyl acetate also gave ^{235}U, which is regarded as isomeric with the short-lived isotope formed by neutron bombardment of U (this vol., 773). These isotopes have the same mass and charge, but differ in nuclear properties. L. S. T.

Mechanism of isotopic exchange reactions. E. OGAWA (Bull. Chem. Soc. Japan, 1936, **11**, 425—427).—Theoretical. Polarisation of atoms probably plays the most impotant part, an element being richer in the heavier isotope when it is in the more positively polarised state. C. R. H.

Arrangement of chemical elements in teaching. E. WIBERG (Angew. Chem., 1936, **49**, 480—481).—A new layout of the periodic table is described, in which the sub-groups and transition elements are introduced between the Ti and Ge sections of group II. J. W. S.

Anchoring of radium emanation on nuclei. G. ALIVERTI and G. ROSA (Atti R. Accad. Sci. Torino, 1934—1935, **70**, I, 266—271; Chem. Zentr., 1935, ii, 2847).—The binding of Rn on nuclei in measurements of atm. radioactivity is improbable; the effect is probably due to Th-Em. J. S. A.

Disintegration constant of thorium and branching ratio of thorium-*C*. A. F. KOVARIK and N. I. ADAMS, jun. (Physical Rev., 1936, [ii], **50**, 99).—By means of a mechanical counter to determine the rate of emission of α-particles from ThO_2 and its products, the ThO_2 being covered with celluloid to prevent escape of Th-Em, the val. of the disintegration const. λ was found to be $5{\cdot}17 \times 10^{-11}$ years^{-1}, the half val. period being $1{\cdot}34 \times 10^{10}$ years. The branching ratio of Th-*C* is 0·660. A. J. M.

Materialisation of the energy of β-rays from radium-*C*. A. M. DA SILVA (Compt. rend., 1936, **202**, 2070—2072).—Data are recorded for the no. of positrons observed in a Wilson chamber with varying thicknesses of Pb surrounding the source. The effects due to the source and to γ- and β-rays are separated. Preliminary experiments with Al screens are described. H. J. E.

γ-Radiation from Po + Be. G. BERNARDINI and L. EMO (Ric. sci. Prog. tec., 1935, II, 6, 17—23; Chem. Zentr., 1935, ii, 2924).—The max. energy of secondary electrons from Po+Be, measured by absorption in Al, is $3{\cdot}5 \times 10^{6}$ e.v. corresponding with γ-rays of $3{\cdot}7 \times 10^{6}$ e.v. J. S. A.

Photon theory and Compton effect. W. Bothe and H. M. Leibnitz (Physical Rev., 1936, [ii], 50, 187).—Investigations showed that the Compton effect for Ra-*C* γ-rays is in agreement with the photon theory, and Shankland's anomalous results (cf. this vol., 265) are not supported but were probably due to inhomogeneity of the γ-rays. N. M. B.

Experimental proof of the diffraction of neutrons. H. von Halban and P. Preiswerk (Compt. rend., 1936, **203**, 73—75).—Data for the angular distribution of neutrons after diffraction through Fe powder at 90° and 300° abs. show that at lower temp. the intensity diminishes and increases for small and large deviations, respectively. C. R. H.

Quantum energy of γ-rays excited by slow neutrons. S. Kikuchi, K. Husimi, and H. Aoki (Nature, 1936, **137**, 992—993).—The absorption curves of the secondary electrons due to γ-rays emitted from 24 elements under bombardment by slow neutrons are discussed. L. S. T.

Neutron. H. A. Shadduck (J. Chem. Educ., 1936, **13**, 303—308).—A summary of recent work. L. S. T.

Neutrality of the neutron. P. B. Moon (Proc. Physical Soc., 1936, **48**, 658).—From the lack of influence of an electric field on neutrons of thermal velocities it is shown that the neutron has no electric charge as great as 10^{-7} of the electronic charge. W. R. A.

Experiments with neutrons having thermal energies. J. R. Tillman (Proc. Physical Soc., 1936, **48**, 642—647).—Different views regarding the influence of temp. on the properties of neutrons are discussed. W. R. A.

Slowing down of neutrons by thin layers of paraffin. S. Nishikawa, S. Nakagawa, and I. Sumoto (Proc. Imp. Acad. Tokyo, 1936, **12**, 128—130).—An analysis of neutron groups was made by passing neutrons through layers of paraffin of various thicknesses and measuring the β-activity induced by the neutrons in Ag and I. Cd filters were also used. A. J. M.

Passage of neutrons through paraffin wax. P. B. Moon (Proc. Physical Soc., 1936, **48**, 648—657).—The velocity distribution of neutrons passing through paraffin wax is investigated on the assumption that the collisions made before thermal velocity has been reached are elastic collisions with protons. The no. of neutrons crossing unit area is investigated and the ratio of the flux of thermal neutrons in the interior to that at the surface is calc. W. R. A.

Diffusion and absorption of neutrons in paraffin spheres. D. M. Yost and R. G. Dickinson (Physical Rev., 1936, [ii], **50**, 128—132).—Measurements were made of the activities imparted to Ag and In detectors in paraffin spheres of various sizes with a Ra–Be source of neutrons at the centre. Results are in fair agreement with theory for distances from the source $>$ 8 cm. The mean free path of the neutrons in paraffin is 0·53 cm., and the ratio of the sp. absorption rate const. to the diffusion const. 0·026 cm.$^{-2}$ N. M. B.

Cross-section measurements with slow neutrons of different velocities. P. Preiswerk and H. von Halban, jun. (Nature, 1936, **138**, 163).—A correction (this vol., 772). L. S. T.

Photo-neutrons. D. P. Mitchell, F. Rasetti, G. A. Fink, and G. B. Pegram (Physical Rev., 1936, [ii], **50**, 189).—The slowing by H_2O of neutrons obtained from the photo-disintegration of Be by Rn γ-rays was investigated, and the growth in no. was compared with that of neutrons from a Rn–Be source. The mean free paths of the Rn γ–Be photo-neutrons and Rn α–Be neutrons were approx. 5 and 9 cm., respectively. The relative no. of photo-neutrons and α-particle neutrons was 0·2 : 1. Similar experiments were made with the Rn bulb in the centre of a 200-c.c. sphere of pure D_2O; the photo-neutrons were much slower, and their no. was 2% of the no. of neutrons from Rn–Be. N. M. B.

Action of neutrons on heavy water. W. F. Libby, E. A. Long, and W. M. Latimer (Physical Rev., 1935, [ii], **47**, 424—425).—Interposition of D_2O between target and source (Rn+Be) results in a large decrease in induced radioactivity. L. S. T.

Scattering of slow neutrons. II. A. C. G. Mitchell, E. J. Murphy, and M. D. Whitaker (Physical Rev., 1936, [ii], **50**, 133—137; cf. A., 1935, 1441; this vol., 541).—Scattering curves are given for neutrons from Fe, Ni, Ag, Cu, and C with various detectors, and the scattering cross-sections for a number of elements are tabulated. Differences in the curves for the Fermi groups are most marked when the scatterer is itself a good absorber of one of the groups. The temp. effect on the neutrons which activate In has been investigated. N. M. B.

Possibility of selective phenomena for fast neutrons. G. Gamow (Physical Rev., 1936, [ii], **49**, 946).—In nuclear transformations due to collisions with fast neutrons, resonance phenomena in the region of semi-light nuclei are predicted, with an indication of fast neutron energy for which resonance disintegration should be observed. The reactions discussed are: ${}^{27}_{13}\mathrm{Al}+{}^{4}_{2}\mathrm{He}\rightarrow{}^{31}_{15}\mathrm{P}\rightarrow{}^{30}_{14}\mathrm{Si}+{}^{1}_{1}\mathrm{H}$; ${}^{25}_{12}\mathrm{Mg}+{}^{4}_{2}\mathrm{He}\rightarrow{}^{29}_{14}\mathrm{Si}\rightarrow{}^{28}_{13}\mathrm{Al}+{}^{1}_{1}\mathrm{H}$; and ${}^{28}_{14}\mathrm{Si}+{}^{1}_{0}n\rightarrow{}^{23}_{14}\mathrm{Si}\rightarrow{}^{28}_{13}\mathrm{Al}+{}^{1}_{1}\mathrm{H}$. N. M. B.

Capture, stability, and radioactive emission of neutrons. J. R. Dunning, G. B. Pegram, and G. A. Fink (Physical Rev., 1935, [ii], **47**, 325).—The no. of neutrons detected in an ionisation chamber 25 cm. distant when a Rn+Be source is placed in the centre of solid spheres of diameters up to 25·7 cm. have been measured for H_2O, C (coal), Al, sand, Cu and Pb shot. The probability of capture indicated is $\not>$ 25% per collision and may be $<$10% for most cases. The disappearance of neutrons is apparently $\not>$ that required by capture in the production of artificial radioactive atoms, by transfer of momentum on impact and by loss of energy in excitation, without supposing the neutron itself to be disintegrated by nuclear impact. L. S. T.

Mass spectrographic determination of the mass difference ${}^{14}\mathrm{N}+{}^{1}\mathrm{H}-{}^{15}\mathrm{N}$ and the nitrogen disintegration reactions. E. B. Jordan and K. T.

BAINBRIDGE (Physical Rev., 1936, [ii], **50**, 98).—The isotopic ion $^{15}N^+$ was matched in intensity with the mol. ion $(^{14}N^1H)^+$. The doublet separations gave the mass difference $^{14}N^1H-^{15}N=0{\cdot}01074\pm0{\cdot}0002$ mass units. The use of this val. together with the previously determined mass difference for $^2_1H-^2D$, gives $8{\cdot}57\pm0{\cdot}2$ m.e.v. for the energy release in the N deuteron disintegration $^{14}N+^2D\rightarrow^{15}N+^1H$. The mass differences in the production of radio-O and in other N disintegration reactions are also calc.
A. J. M.

Proton emission resulting from α-ray bombardment of boron and phosphorus. R. F. PATON (Physical Rev., 1935, [ii], **47**, 197).—When bombarded with α-particles from Th-*C′* the protons emitted from B consist of ≮ four groups with characteristic velocities and energies, the vals. for three of which agree with those obtained using Po α-particles. With P, new proton groups are emitted.
L. S. T.

Selection rules for the β-disintegration. G. GAMOW and E. TELLER (Physical Rev., 1936, [ii], **49**, 895—989).—The rules are stated on the basis of Fermi's neutrino theory. N. M. B.

Decomposition of beryllium under influence of γ-rays. G. BERNARDINI and M. MANDÒ (Ric. sci. Prog. tec., 1935, **6**, II, 38—41; Chem. Zentr., 1935, ii, 2627).—If a Be isotope ^8_4Be+a neutron are formed by the γ-ray disintegration of ^9_4Be, the isotope must either be stable, or else emit α-rays of range ≯ 2·5 mm. J. S. A.

Fermi proton effect. A. VON GROSSE and M. S. AGRUSS (Physical Rev., 1935, [ii], **47**, 91).—Filling a Ag cup with H_2O increases the activity produced in the Ag by irradiation with neutrons from Be+Rn. Surrounding the cup with H_2O increases the activity still further. *n*-C_5H_{12} has a similar effect, but not CCl_4 or CS_2. The addition of 5% of $UO_2(NO_3)_2$ or H_3BO_3 to the H_2O reduces the effect. The protons of the H_2O absorb the energy of the neutrons by elastic collisions, and the neutrons are then more easily captured with the production of stable or radioactive isotopes. L. S. T.

γ-Ray neutrons and the Fermi proton effect. A. VON GROSSE and M. S. AGRUSS (Physical Rev., 1935, [ii], **47**, 93).—Neutrons emitted by γ-rays from Be show the Fermi proton effect. Irradiation of I by Be+γ-rays from Ra gives a product with a half-period of 24 min. Surrounding the source with H_2O increases the induced radioactivity five-fold (cf. preceding abstract). L. S. T.

Disintegration of beryllium by photons and its possible bearing on the mass of ^{9}Be. L. N. RIDENOUR, K. SHINOHARA, and D. M. YOST (Physical Rev., 1935, [ii], **47**, 318).—Bombardment of Be with *X*-rays at 50 cycle a.c. at 0·9 m.e.v. gives results which indicate that the mass of ^{9}Be is too high. A val. of 9·0114 is calc. L. S. T.

Evidence from efficiency curves for the nature of the disintegration process for boron. J. H. WILLIAMS and W. H. WELLS (Physical Rev., 1936, [ii], **50**, 186—187).—Efficiency curves for the production of α-particles by bombarding a B_2O_3 thick target with protons of 120—240 kv. are given and discussed. The suggested reaction $^1_1H+^{11}_5B\rightarrow^8_4Be+^4_2He$ is probably a case of resonance disintegration. N. M. B.

Ranges of particles emitted in the disintegration of boron and lithium by slow neutrons. J. ROTBLAT (Nature, 1936, **138**, 202).—The ranges of particles emitted during disintegration of ^{10}B and ^{6}Li by slow neutrons from a Po–Be source, using a B- or Li-coated ionisation chamber, have been determined, and the energies calc. An additional release of energy from B, possibly related to γ-rays, is indicated. The cross-section of the B nucleus for capture of a slow neutron is 8 times that of the Li nucleus. L. S. T.

Absorption and scattering of neutrons. W. F. LIBBY and W. M. LATIMER (Physical Rev., 1935, [ii], **47**, 193).—Interposition of H_2O between a Ag target and the neutron source (Be+Rn) markedly increases the activation induced. H_3BO_3 decreases the activation of Ag and Cu, as do KCl, NaCl, CCl_4, and $BiONO_3$ with Cu. Absorption with NaF, NaI, BeO, and CuO is negligible, and NH_4NO_3 and S produce small increases in activation. L. S. T.

Bifurcation in the transmutation of aluminium by the action of fast neutrons. P. DE LA CIERVA (Anal. Fís. Quím., 1936, **34**, 541—548).—The no. of atoms of Al transformed into ^{27}Mg to every atom transformed into ^{24}Na, on bombardment with neutrons from different sources, is as follows: Be+Rn source, 2·1; Be+Ra, 3·2; Be+Ra, with Pb between Al and neutrons, 3·23; Be+Ra, with paraffin interposed, 3·09 (also forms ^{28}Al); Li+Rn, no ^{27}Mg or ^{24}Na, but ^{28}Al; Mg+Rn, only ^{27}Mg. L. A. O'N.

Artificial radioelements. M. E. NAHMIAS and R. J. WALEN (Compt. rend., 1936, **203**, 71—73).—Evidence has been obtained for the formation of ^{20}F, ^{19}O, and ^{16}N from F, and ^{20}F and ^{23}Ne from Na, as a result of neutron bombardment. With periods of the order of 1 sec. the results are inconclusive, but the activation of Be is confirmed, ^{9}Li probably being formed. C. R. H.

Disruption of atoms by neutrons. E. MATZNER (Sitzungsber. Akad. Wiss. Wien, 1934, **143**, 579—590; Chem. Zentr., 1935, ii, 2628).—The yields obtained by the neutron disintegration of C, Al, S, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Pt, and Pb have been measured by scintillation and Wilson chamber methods. J. S. A.

Disruptibility of light elements investigated with the double-tube electrometer. J. SCHINTLMEISTER and G. STETTER (Sitzungsber. Akad. Wiss. Wien, 1934, **143**, 597—617; Chem. Zentr., 1935, ii, 2629).—The disintegration yield of the light elements up to Cl shows an exponential fall from a max. in the case of N, on which is superposed a periodic function giving a uniformly higher yield from "odd" elements than from "even." J. S. A.

Radioactive isotope of iron. E. B. ANDERSEN (Nature, 1936, **138**, 76—77).—Active Fe, probably $^{59}_{26}Fe$, decaying with a period of approx. 72 hr. has been isolated from Co irradiated by neutrons.
L. S. T.

Artificial activation of thorium by neutrons. E. Rona and E. Neuninger (Naturwiss., 1936, **24**, 491).—By bombardment of pure $ThCl_4$ with slow and rapid neutrons, products were obtained with half-life periods of 25 min. (isotope of Th), 3·5 hr. (isotope of Ac), and 42 hr. (isotope of Ac). The most probable scheme of disintegration is $^{232}_{90}Th+^{1}_{0}n=^{229}_{88}Ra+^{4}_{2}\alpha$; $^{229}_{88}Ra\xrightarrow{\beta}{}^{229}_{89}Ac\xrightarrow{\beta}{}^{229}_{90}Th\xrightarrow{\beta}{}^{229}_{91}Pa\xrightarrow{\alpha}{}^{225}_{88}Ac\xrightarrow{\beta}{}^{225}_{90}Th$. A. J. M.

Energy of cosmic rays. I. Electro-magnet and cloud chamber. P. M. S. Blackett. **II. Curvature measurements and the energy spectrum.** P. M. S. Blackett and R. B. Brode (Proc. Roy. Soc., 1936, A, **154**, 564—573, 573—587).—I. Details are given of a large cloud chamber in a strong magnetic field, for measuring high-energy cosmic ray tracks.

II. The sources of error are considered, and a preliminary determination of the energy spectrum of 188 vertical cosmic rays is made. L. L. B.

Frequency of secondary phenomena of the radiation penetrating lead. A. Drigo (Ric. sci. Prog. tec., 1935, I, 6, 529—534; Chem. Zentr., 1935, ii, 2925).—Measurements of the dependence of the no. of particles on the thickness of the absorbing screens do not support Rossi's views (A., 1935, 804). J. S. A.

Origin of the hardening of cosmic rays in passing through matter. W. F. G. Swann (Physical Rev., 1935, [ii], **47**, 250). L. S. T.

Production of cosmic-ray showers. W. H. Pickering (Physical Rev., 1935, [ii], **47**, 423). L. S. T.

Bursts of cosmic radiation. A. R. Hogg (Nature, 1936, **138**, 77—78). L. S. T.

Critique of daily course of cosmic radiation. A. Wagner (Sitzungsber. Akad. Wiss. Wien, 1934, **143**, 533—561; Chem. Zentr., 1935, ii, 2629—2630).—Data recorded previously are analysed. J. S. A.

Electrostatic deflexion of cosmic radiation. W. E. Danforth and W. F. G. Swann (Physical Rev., 1935, [ii], 47, 421). L. S. T.

Influence of earth's magnetic field on penetrating radiation in geographical latitude of Florence. G. Bernardini and D. Bocciarelli (Ric. sci. Prog. tec., 1935, 6, II, 36—37; Chem. Zentr., 1935, ii, 2630). J. S. A.

Form of nuclear levels [of rhodium]. P. Preiswerk and H. von Halban, jun. (Nature, 1936, **138**, 163). L. S. T.

Self-consistent field, with exchange, for beryllium. II. The $(2s)(2p)^3P$ and ^1P excited states. D. R. Hartree and W. Hartree (Proc. Roy. Soc., 1936, A, **154**, 588—607; cf. A., 1935, 912).—Foch's equations for the self-consistent field, including exchange terms, have been obtained and solved numerically for the $(2s)(2p)^3P$ and ^1P terms of neutral Be. The calc. energy vals. are in agreement with observation. L. L. B.

Present state of the neutrino hypothesis. G. Beck (Physical Rev., 1935, [ii], **47**, 202).—A discussion. The hypothesis does not remove difficulties arising from experimental evidence. L. S. T.

Mass and energy. K. Wagner (Physikal. Z., 1936, **37**, 522—523).—It is not necessary to regard the relationship between mass and energy as a relativistic conception. It follows from Maxwell's work on the pressure of light. A. J. M.

Nuclear structure and isotope systems. T. I. Efremenko (Ukrain. Chem. J., 1936, **11**, 103—118).—Theoretical. R. T.

Nomenclature of elementary corpuscles. P. Gruner (Helv. phys. Acta, 1935, 8, 326—327; Chem. Zentr., 1935, ii, 2923).—For the electrical particles (electrons) the names positon, negaton, and nulliton (uncharged) are proposed. Material particles (materions) are termed neutrons, protons, deutons, tritons, etc., with neproton as a negative particle of mass 1. J. S. A.

Extended Thomas–Fermi method for atomic nuclei. F. S. Wang (Z. Physik, 1936, **100**, 734—741). A. B. D. C.

Nuclear radius. A. K. Solomon (Physical Rev., 1935, [ii], 47, 249).—For both light and heavy nuclei, the nuclear radius ∝ the cube root of the at. wt. of the product nucleus. The slopes of the lines for heavy and light elements are parallel. When the nuclear radius is plotted against at. no. a random distribution of radioactive nuclei is obtained. L. S. T.

Value of the electronic charge. R. T. Birge and E. McMillan (Physical Rev., 1935, [ii], **47**, 320; cf. this vol., 133, 404).—A discussion and recalculation of Schopper's val. (A., 1935, 279). L. S. T.

Conservation laws in quantum theory. N. Bohr (Nature, 1936, **138**, 25—26).—Doubts concerning the validity of conservation of energy and momentum in at. phenomena are now largely removed. The root of the still unsolved difficulties of quantum electrodynamics lies in the atomistic nature of electricity. L. S. T.

Atomic collisions and radiation from meteors. E. Öpik (Acta Univ. Tartuensis, 1934, **26**, A, No. 2, 37 pp.; Chem. Zentr., 1935, ii, 2798).—Theoretical. J. S. A.

Absorption spectra of iodine solutions. II. Influence of iodide. A. V. Pamfilov and R. V. Teis (J. Gen. Chem. Russ., 1936, **6**, 588—605).—Progressive dilution of I in KI solutions with aq. KI leads to a shift in the position of the absorption bands and to diminution in intensity of coloration; these changes are reversed by further addition of aq. KI. Similar effects are obtained in presence of starch. Beer's law is followed more closely when the solution is diluted with H_2O than with aq. KI. The effects are ascribed to the existence of a series of equilibria between I, KI, KI_3, and H_2O. R. T.

Induced pre-dissociation and energy exchange in nitric oxide. E. Kondrateeva and V. Kondrateev (Acta Physicochim. U.R.S.S., 1935, **3**, 1—10).—

The ratio of intensities of the β- and γ-bands in the emission spectrum of NO alone and when mixed with A has been determined. In the spectrum of pure NO the γ-bands are much more intense than the β-bands, but in that of the mixture they are of approx. equal intensity. The phenomena can be explained on the hypothesis of induced pre-dissociation in the $^2\Sigma$ state. The probability of the transfer of a quantum of vibrational energy of an excited NO mol. into kinetic energy on collision with an A atom is calc. to be approx. 1. A. J. M.

Band spectra of boron and aluminium halides. E. Miescher (Helv. phys. Acta, 1935, **8**, 279—308; Chem. Zentr., 1935, ii, 2633).—Emission spectra from BCl_3 vapour between 2600 and 2900 A. and from BBr_3 vapour between 2850 and 3100 A. are analysed and referred to $^1\Pi \rightarrow {}^1\Sigma$ transitions. Similar $^3\Pi \rightarrow {}^1\Sigma$ bands excited in $AlBr_3$ and AlI_3 are described. Dissociation energies are calc. J. S. A.

Ultra-violet band systems of SiCl. W. Jevons (Proc. Physical Soc., 1936, **48**, 563—573).—The emission spectrum of SiCl, produced from $SiCl_4$ vapour, has three systems of doublet bands degraded towards the further ultra-violet. The bands are discussed and compared with the data of Datta. W. R. A.

Absorption spectrum of tellurium dichloride vapour. J. Larionov (Acta Physicochim. U.R.S.S., 1935, **3**, 11—22).—The absorption spectrum of $TeCl_2$ has been investigated in the visible and ultra-violet. The bands in the visible may be classified into three sequences, the spectrum being made up of broad diffuse bands without heads with a superimposed continuous absorption. There is a further continuous absorption in the ultra-violet. The first continuous absorption in the visible may be due to $TeCl_2 + h\nu \rightarrow TeCl + Cl$; $TeCl_2 + h\nu \rightarrow TeCl + Cl'$; or $TeCl_2 + h\nu \rightarrow Te + Cl_2$. The corresponding heats of dissociation for these processes are 54, 56, and 51 kg.-cal., respectively. A. J. M.

Emission spectrum of bismuth fluoride. H. G. Howell (Proc. Roy. Soc., 1936, **A**, **155**, 141—150).—An emission spectrum attributed to BiF has been excited by means of a high-frequency discharge in the vapour of BiF_3. The bands lie in the region 4150—5100 A. and are degraded to the red. A vibrational analysis has been made. The vibrational consts. are nearly equal to those of PbF. L. L. B.

Change in the absorption spectrum of cobalt chloride in aqueous hydrochloric acid solution with change of temperature. O. R. Howell and A. Jackson (Proc. Roy. Soc., 1936, **A**, **155**, 33—41).—The absorption spectra of several aq. solutions containing a fixed amount of $CoCl_2$ and varying amounts of HCl have been measured at a series of temp. The extinction coeffs. at the max. of the two principal bands, 695 mμ and 666 mμ, have been plotted against temp. For a given [HCl], the extent of the transformation from red to blue over a wide range of temp. is small compared with the total change observed on increasing [HCl] at const. temp. The results are explained in terms of the theory previously advanced (A., 1934, 7). L. L. B.

New absorption band in potassium bromide crystals. E. Rexer (Physikal. Z., 1936, **37**, 523).—Electron migration in a KBr crystal may produce absorption bands which do not give rise to photochemical processes. A KBr crystal, heated for some time in air, gives an absorption band due to electron migration with a max. at 302 mμ. Absorption in this band does not give rise to photochemical colouring, but to the emission of fluorescence with a max. at 453 mμ. A. J. M.

Band spectrum of FeH. A. Heimer (Naturwiss., 1936, **24**, 491—492).—The strongest band in the spectrum of FeH is the 0—0 band at 4288 A. It is degraded towards the red, and consists of single *P* and *R* branches. It arises from a $^1\Sigma - {}^1\Sigma$ transition. A. J. M.

The 2530 A. band of NH. R. W. Lunt, R. W. B. Pearse, and E. C. W. Smith (Proc. Roy. Soc., 1936, **A**, **155**, 173—182).—The 2530 band of NH has been excited by a hollow-cathode discharge in streaming NH_3 with sufficient intensity to photograph under high dispersion. The band corresponds with a $^1\Sigma^+ \rightarrow {}^1\Pi$ transition, and the $^1\Pi$ state is the same as that already known as the initial state concerned in the emission of the 3240 and 4502 bands. The rotational consts. for the six electronic states now known for NH are tabulated. L. L. B.

Absorption of light by some gases in the far ultra-violet. G. Rathenau (Physica, 1936, **3**, 727—728).—NH_3, N_2, N_2O, CO_2, and C_6H_6 show continuous absorption in the region 150—270 A. O. D. S.

Band spectrum of OH⁺. M. Kovner (Physical Rev., 1936, [ii], **50**, 188; cf. Loomis, this vol., 267).—Term differences and multiplet splitting consts. are evaluated. N. M. B.

Band spectrum of arsenic oxide (AsO) and lead oxide (PbO). F. Morgan and E. N. Shawhan (Physical Rev., 1935, [ii], **47**, 192—199).—The band spectrum of AsO has been studied in emission and absorption and that of PbO in absorption. L. S. T.

Absorption spectra and photodissociation of some inorganic molecules. M. Jan-Khan and R. Samuel (Proc. Physical Soc., 1936, **48**, 626—641).—The regions of absorption in PCl_3, PBr_3, PCl_5, PBr_5, $POCl_3$, P_2O_5, $AsCl_3$, $SbCl_3$, SbOCl, and $BiCl_3$ are correlated with certain photodissociation processes. A comparison with the mean bond energies calc. from thermochemical data allows certain conclusions to be reached as to the structure of these mols. W. R. A.

Absorbing and reflecting powers of sulphuric acid solutions in the far infra-red. C. H. Cartwright (J. Chem. Physics, 1936, **4**, 413—417).—Measurements are recorded with 2—37·4*N*-H_2SO_4 for λλ 52—152 μ monochromatic. A broad absorption band at approx. 60 μ, similar to the 60 μ band of H_2O, was observed in dil. and conc. H_2SO_4. This appears to be of interat. origin. The reflecting and absorbing powers of aq. H_2SO_4 are ≫ those of H_2O or H_2SO_4. It is suggested that with < 5% of H_2O in H_2SO_4, SO_4'' and $OH_3^{\cdot\cdot}$ ions may be formed.

On further dilution H˙ and H_3SO_4' are formed. In dil. solutions H˙ and SO_4'' are present. H. J. E.

Far ultra-violet absorption spectrum of methyl iodide. W. C. Price (Physical Rev., 1935, [ii], **47**, 419).—Analysis of this spectrum at low pressures in the region 2000—1200 A. gives two ionisations potentials, viz., 9·489 and 10·113 volts(±0·003 volt). L. S. T.

Absorption spectrum of alkyl iodides in extreme quartz ultra-violet. I. Experimental. G. Milazzo (Z. physikal. Chem., 1936, **B**, **33**, 109—119).—The v.p. and absorption spectra of the saturated vapours of PrI, BuI, $Pr^\beta I$, and $Bu^\gamma I$ have been measured at various temp. as far as 1960 A. R. C.

Electronic state of radicals in polyatomic molecules. V. Henri (Compt. rend., 1936, **203**, 67—69).—The CN group in cyanides and thiocyanates is in the normal inactive state $X(^2\Sigma)$ and in halogen derivatives and carbylamines it is in the active state $B(^2\Sigma)$. In nitriles it appears to be in a higher state than those known, the frequency being approx. 2250 cm.$^{-1}$ The groups C⋮C, N⋮N, and NO are, respectively, in the states $A(^3\Pi)$, $C(^3\Pi)$, and $X(^2\Pi)$. C. R. H.

Tetramethylethylene and the influence of the double linking. J. Errera, P. Mollet, and (Mlle.) M. L. Sherrill (Compt. rend., 1936, **203**, 66).—The positions of the spectral absorption bands for C_2Me_4 are discussed in relation to the band positions of saturated and ethylenic hydrocarbons (cf. this vol., 1049). C. R. H.

Ultra-violet absorption of some aromatic hydrocarbons. IV. Constitution of hexahydropyrene. M. Pestemer and F. Manchen (Monatsh., 1936, **68**, 92—100).—The absorption spectrum of hexahydropyrene (I) (2500—4500 A.) resembles those of $C_{10}H_8$ and its alkyl derivatives. It is concluded that (I) contains an intact $C_{10}H_8$ ring system and that hydrogenation occurs symmetrically in the two remaining rings in the mol. The partly hydrogenated products obtained by the action of nascent H have absorption spectra corresponding with mixtures of (I) and pyrene. H. J. E.

Variations in the ultra-violet spectrum of phenol as a function of p_H. M. Gex (Compt. rend., 1936, **202**, 2145—2147).—The ultra-violet absorption of PhOH solutions of varying p_H indicates that on passing from PhOH to phenoxide an intermediate modification of PhOH exists between p_H 7 and 9. C. R. H.

Ultra-violet absorption by liquids. L. A. Ginsel (Physica, 1936, **3**, 578—584).—Preliminary. Qual. diagrams of the ultra-violet absorption bands of *o*- and *m*-$C_6H_4Cl\cdot OH$ and $PhNO_2$ are given. O. D. S.

Absorption spectra of hydroxyanthraquinones in different solvents. K. Lauer and M. Horio (J. pr. Chem., 1936, [ii], **145**, 273—280).—Absorption spectra of 1- (I) and 2-hydroxy- and 1 : 8-, 1 : 3-, 1 : 6-, 2 : 3-, 2 : 6-, and 2 : 7-dihydroxy-anthraquinone in C_6H_6, *cyclo*hexane, EtOH, conc. H_2SO_4, and aq. NaOH are detailed. The OH gives a band with max. about 4000 A., shifted for all compounds except (I) by H_2SO_4 and NaOH to about 5000 A. or higher λ; with (I) only NaOH causes this shift. The absorption max. of 1- and 2-aminoanthraquinone move to higher λ with increasing ε of the solvent, in contradiction to Scheibe's rule. R. S. C.

Behaviour of the absorption band of uranine solution under high pressure. W. J. Lyons (Physical Rev., 1935, [ii], **47**, 198).—For pressures up to 915 kg. per sq. cm., the absorption band max. of a dil. aq. solution of uranine did not show the expected shift to regions of longer λ. L. S. T.

Substitution and absorption-band displacement. VII. Anthracene and naphthalene derivatives. H. Conrad-Billroth (Z. physikal. Chem., 1936, **B**, **33**, 133—144; cf. A., 1935, 913).—The application of the rule previously described (A., 1933, 445) to the above compounds is examined. The absorption bands consist of two groups, the position of which in the unsubstituted mols. is characterised by a zero point common to both ring systems and by two " ring-fusion influence vectors " which in substitution are included in the geometrical addition. These lie in the plane of the mol. and in the axis of symmetry. The direction of the substituent " influence vectors " is towards the centre of the ring system, not the centre of single rings. With these modifications the rule is valid. R. C.

Spectroscopic studies of the simpler porphyrins. I. Absorption spectra of porphin, *ms*-methyl-, -ethyl-, -propyl-, and -phenylporphin. V. M. Albers and H. V. Knorr (J. Chem. Physics, 1936, **4**, 422—425).—Curves for the mol. absorption coeffs. of Et_2O solutions for λλ 3700—7000 A. are recorded. There is a very strong band at 3900 A. in porphin, at 4130 A. in all the aliphatic-substituted mesoporphins (I), and at 4140 A. in *ms*-phenylporphin. For (I) the absorption coeff. for this band decreases as the length of the C chain increases. Beer's law holds. H. J. E.

Fluorescence of the porphyrins. III. A. Stern and M. Deželić (Z. physikal. Chem., 1936, 347—357).—The fluorescence spectrum of solutions of octaethylporphin (I) varies little with the solvent, the band max. being shifted towards the blue compared with those of solid (I). The spectrum of adsorbed (I) has its max. in approx. the same position as that of a HCl solution, indicating that adsorption involves primarily the N atoms of the pyrrolenine nuclei, and these in a similar way to salt formation. Hen- and duck-egg shells give similar spectra, showing the same porphyrin, ooporphyrin (II), to be present in each. The (II) is present in the shell in mol. solid solution, not in the adsorbed state, for the spectra resemble that of protoporphyrin in neutral solution. R. C.

Absorption spectrum of bilirubin. J. Henry-Cornet and L. A. M. Henry (Bull. Acad. roy. Belg., 1936, [v], **22**, 553—559).—There is a max. in the absorption spectrum of bilirubin between 2300 and 3800 A., made up of a no. of max. and min. The absorption spectrum is characteristic and may be used to identify the substance. Determination of the extinction const. may be used to measure the concn. of bilirubin in serum. A. J. M.

Conditions for excitation of fluorescence of proteins. F. Vlès (Compt. rend., 1936, **202**, 2184—2186).—The fluorescence of certain proteins and NH_2-acids when subjected to ultra-violet light is described. C. R. H.

Influence of van der Waals forces on energy states of molecules on basis of luminescence of solidified gases. L. Vegard (Avh. norsk. Vid.-Akad. Oslo, 1935, No. 2, 14 pp.; Chem. Zentr., 1935, ii, 2783; cf. A., 1935, 147).—The fluorescence bands of solid N_2–inert gas mixtures are broadened towards longer λλ by van der Waals forces. Electronic terms are affected to a greater extend than vibrational terms. J. S. A.

Photographic infra-red absorption spectrum of gaseous ammonia. S. H. Chao (Physical Rev., 1936, [ii], **50**, 27—37).—The absorption bands of NH_3 at 10,000, 7920, and 6470 A. have been re-investigated using apparatus with greater dispersion and resolving power. Some difficulty was experienced in analysing the bands, the complexity of structure being probably due to the fact that the bands are made up of several parallel-type and perpendicular-type bands. The effect of pressure on the width of the lines is considerable, but in mixtures of NH_3 and air, increase of air pressure produced only slight broadening. The broadening with increase of pressure may be due to the intermol. Stark effect connected with the dipole moments of the mols. A. J. M.

Near infra-red spectrum of MgO. R. B. Barnes and R. R. Brattain (Physical Rev., 1935, [ii], 47, 416). L. S. T.

Infra-red spectrum of heavy acid solutions. D. Williams and E. K. Plyler (J. Chem. Physics, 1936, 4, 460).—D_2O solutions of DCl, D_2SO_4, and D_3PO_4 have absorption bands at 5·7 and 3·4 μ. H. J. E.

Infra-red spectra and organic chemistry. R. B. Barnes (Rev. Sci. Instr., 1936, [ii], 7, 265—271).—A general survey of applications to deuterochemistry, polymerisation, isomerism, tautomerism, detection of H linkings, qual. analysis, and determination of particle size. N. M. B.

Effect of association on the infra-red absorption spectrum of acetic acid. R. H. Gillette and F. Daniels (J. Amer. Chem. Soc., 1936, **58**, 1139—1142).—The infra-red absorption spectrum has been obtained at 25° and 172°, corresponding with single and associated mols., respectively. Three of the fundamental frequencies are the same in both mols., and two are shifted. Modes of vibration of the two mols. are suggested. The association of carboxylic acids to dimerides probably occurs through the formation of H linkings leading to ring structure, which gives rise to different absorption frequencies. E. S. H.

Effect of substitution on the infra-red absorption spectrum of acetic acid. R. H. Gillette (J. Amer. Chem. Soc., 1936, 58, 1143—1144).—Uniform shifts in the infra-red absorption spectra of AcOH and mono-, di-, and tri-chloro-, mono-bromo- and -iodo-, di-, and tri-methyl-, and diethyl-acetic acid have been determined. E. S. H.

[Absorption] spectra in the near infra-red. Methane and its chloro- and nitro-derivatives. C. Corin (J. Chim. phys., 1936, **33**, 448—475).—Absorption bands between 0·8 and 2·7 μ are listed for Pr$^{\alpha}$OH, Pr$^{\beta}$OH, allyl alcohol, glycerol, EtCHO, C_2H_3·CHO, $COMe_2$, $EtCO_2H$, C_2H_3·CO_2H, $AcCO_2H$, NEt_3, $NHEt_2$, NH_2Et, nitrosodipropylamine, and EtONO. Liquid CH_4 has a band at 2·0 μ not present in the vapour. The absorption of the Cl-derivatives of CH_4 diminishes as the no. of C·H linkings decreases. CCl_3·NO_2 has 7 bands at 1·40—2·59 μ at λλ identical with those of $C(NO_2)_4$. Frequencies are allocated to the CH, NO, C·NO_2, and NO_2 groupings. J. G. A. G.

Photometric and spectrophotometric studies. XI. Absorption spectra of hydrocarbons and halogen derivatives in the near infra-red. E. Trabert and K. Schaum (Z. wiss. Phot., 1936, **35**, 153—170).—The absorption spectra in the near infra-red of the following compounds are recorded: the normal paraffins, C_nH_{2n+2} (n=5—9), EtBr, EtI, Pr$^{\alpha}$Cl, Pr$^{\beta}$Cl, Pr$^{\alpha}$Br, Pr$^{\beta}$Br, Bu$^{\alpha}$Cl, Bu$^{\alpha}$Br, Bu$^{\beta}$Cl, Bu$^{\beta}$Br, $CHCl_3$, $CHBr_3$, C_6H_6, $C_{10}H_8$, phenanthrene, Ph_2, CH_2Ph_2, $CHPh_3$, *cyclo*-hexane and -hexene, tetra- and deca-hydronaphthalene, PhMe, *m*-xylene, 1 : 3 : 5-$C_6H_3Me_3$. A. J. M.

Infra-red absorption of liquid hydrocarbons. Influence of the double linking. J. Errera, P. Mollet, and (Mlle.) M. L. Sherrill (Compt. rend., 1936, **202**, 2141—2142).—Variations in infra-red absorption of saturated and unsaturated aliphatic hydrocarbons are described. C. R. H.

Infra-red absorption of rubber and related hydrocarbons. D. Williams (J. Chem. Physics, 1936, 4, 460).—Very thin films of styrene, isoprene, and cymene all show intense absorption bands at λλ 3·4, 6·2, and 7·0 μ and weaker bands between 7 μ and 9 μ. Pure gum rubber gave a band at 5·8 μ and in a low-S vulcanised rubber the corresponding absorption was at 6·0 μ. At all other λλ from 2·5 to 9·0 μ the absorption spectrum of rubber resembles that of isoprene. Polymerised butadiene gave strong bands at 5·5 and 6·0 μ and less intense bands beyond 7 μ. Rubber hydrochloride gave a very intense band at 8·4 μ, which was not characteristic of the other hydrocarbons studied. H. J. E.

Evidence from Raman effect for a slight asymmetry of the carbon atom. R. T. Dufford (Physical Rev., 1935, [ii], 47, 199).—The Raman spectra of many simple C compounds afford evidence of two slightly different strengths of linking. Similar but less extensive evidence exists for O and N. L. S. T.

Raman spectra of N_3^-, NCS^-, and CO_2. A. Langseth and J. R. Nielsen (Physical Rev., 1935, [ii], 47, 198).—A further study (cf. A., 1935, 145) and application to the constitution of N_3^- and CNS^-. New measurements of the depolarisations and relative intensities of the principal Raman bands of CO_2 have been made. L. S. T.

Raman effect of water vapour. D. Bender (Physical Rev., 1935, [ii], **47**, 252).—H_2O vapour at 135° excited by Hg 2536 A. gives only one Raman band 3654·5 cm.$^{-1}$ and extending approx. 5 cm.$^{-1}$ on both sides of its centre. There is no indication that the line is double (cf. A., 1934, 1155). No pure rotation band was found. L. S. T.

Raman spectra. III. Deuterium-substituted acetic acids. W. R. Angus, A. H. Leckie, and C. L. Wilson (Proc. Roy. Soc., 1936, A, **155**, 183—194).—The Raman spectra of Ac_2O, AcOH, AcOD, and $CD_3{\cdot}CO_2D$ have been studied. Ac_2O exhibits some lines not found in the spectra of the acetic acids. The lines of the acids are divisible into three categories: those unmodified on D substitution, those showing a progressive modification as the D content is increased, and those modified in $CD_3{\cdot}CO_2D$ only. This classification leads to the assignment of the most prominent frequencies. That corresponding with the symmetrical C–D vibration is 2111 cm.$^{-1}$, and with the CD_2 group 1100 cm.$^{-1}$ L. L. B.

Raman spectra of the deuteromethanes. G. E. MacWood and H. C. Urey (J. Chem. Physics, 1936, **4**, 402—406).—MeD, CH_2D_2, CHD_3, and CD_4 were prepared by the interaction of MeI, CH_2I_2, and $CHBr_3$ with D_2O with a Al–Hg couple and by interaction of CO_2 and D_2 with a supported Ni catalyst at 310°, respectively. The first three substances were studied at a pressure of 2 atm., and the last-named at 5 atm. 20 lines were measured and analysed. Rotational structure of CD_4 was observed. H. J. E.

Raman spectrum of *cyclo*propane. R. Ananthakrishnan (Nature, 1936, **138**, 123).—Data for the liquid and vapour are compared and discussed; those for the liquid include new frequencies at 736, 1503, 2852, and 2952 cm.$^{-1}$ L. S. T.

Raman spectra of some substituted epoxy*cyclo*hexanes. E. Canals, M. Mousseron, L. Souche, and P. Peyrot (Compt. rend., 1936, **202**, 2084—2086).—Data are recorded for epoxy*cyclo*hexane and various alkyl and aryl derivatives. They are compared with corresponding vals. for *cyclo*hexane. H. J. E.

Raman spectrum of some substituted epoxy*cyclo*pentanes. E. Canals, M. Mousseron, L. Souche, and P. Peyrot (Compt. rend., 1936, **202**, 1989—1992).—Data for a series of derivatives are recorded and discussed. H. J. E.

Raman spectrum of indole. G. B. Bonino and R. Manzoni-Ansidei (Ric. sci. Prog. tecn., 1935, **6**, I, 579—580; Chem. Zentr., 1935, ii, 3082).—The spectrum contains the lines of a C-disubstituted pyrrole and of an *o*-disubstituted C_6H_6, confirming the chemical formulation as a pyrrole ring fused to a C_6H_6 ring. H. N. R.

Raman spectrum of divinyl sulphide. G. B. Bonino, R. Manzoni-Ansidei, and D. Dinelli (Ric. sci. Prog. tecn., 1935, **6**, I, 505—506; Chem. Zentr., 1935, ii, 3081—3082).—The spectrum is compared with those of thiophen and diallyl sulphide. Conjugation of the S with the C:C linking shifts the C:C line from 1630—1650 cm.$^{-1}$ to 1580—1590 cm.$^{-1}$ The absence of such a line in thiophen points to the absence of C:C linkings. A similar shift in compounds containing a C:C conjugated with a C_6H_6 ring cannot be taken as evidence for the validity of the Kekulé structure. H. N. R.

Raman spectrum of pyrrole and its derivatives. G. B. Bonino (Gazzetta, 1936, **66**, 316—336).—Theoretical; a recent paper by Stern and Thalmayer (this vol., 546) is discussed and criticised. E. W. W.

Electrical resistance of cadmium films. E. Townes and D. Roller (Physical Rev., 1935, [ii], **47**, 197).—Cd films deposited on a glass plate cooled by liquid air or solid CO_2 in a mol. beam apparatus become conducting at a thickness of $2—7\times10^{-7}$ cm. and have a crit. thickness of $6—8\times10^{-7}$ cm., at which the resistivity is approx. 15 times that of the bulk metal. The bearing of these results on photo-electric phenomena in metal films and on theories of film structure is discussed. L. S. T.

Electrical properties of anodically oxidised aluminium. J. W. Holst (Tids. Kjemi, 1936, **16**, 73—76; cf. this vol., 565).—The dry Al_2O_3 layer has low electrical conductivity, only slightly unidirectional, probably due to presence of $Al(OH)_3$. It is concluded that the rectifying properties of the oxidised Al electrode cannot be due to a pure electron flow through the oxide layer. M. H. M. A.

Crystal photo-effect and rectifying action in the bulk of the crystal. G. Groetzinger and J. Lichtschein (Nature, 1936, **138**, 163—164).—Illumination of a cuprite crystal in contact with two electrodes through which an a.c. is passing produces an additional direct voltage. Curves showing the variation of this voltage with the a.c. and its relation to the crystal photo-electric effect are given. The additional current is probably connected with events occurring in the interior of the crystal (bulk rectification). L. S. T.

Contact potential differences between single crystal surfaces of different orientations. I. H. Kurzke and J. Rottgardt (Z. Physik, 1936, **100**, 718—725).—The contact p.d. between the (111) and the (111) planes of a single Bi crystal is +0·36 volt. A. B. D. C.

Influence of atmospheric gases on the electrical conductivity of cuprous oxide. L. Dubar (Compt. rend., 1936, **203**, 46—48).—The influence of dry O_2, dry N_2 (O_2-free), and H_2O vapour on the surface κ of Cu_2O, which has been heated in vac., has been studied. N_2 and H_2O vapour have little effect, but O_2 increases κ. Subsequent treatment with N_2 or H_2O reduces κ to its original val. C. R. H.

Recent investigations of semi-conductors. A. Schulze (Chem.-Ztg., 1936, **60**, 545—547).—A review of literature concerning Si, C, Ti, Zr, Hf, Th, B, As, and Te. T. G. P.

Theory of non-independent flow of electricity in gases. H. Mache (Elektrotech. u. Maschinenbau, 1935, **53**, 253—258, 269—273; Chem. Zentr., 1935, ii, 2784).—Theoretical. An approx. theory is developed and applied to the calculation of the discharge characteristics of condensers with nonhomogeneous ionisation. J. S. A.

Dielectric losses in a high-frequency alternating field and molecular dimensions. J. Henrion (Compt. rend., 1936, **203**, 52—54).—Data for high-frequency dielectric losses for polar mols. in a non-polar solvent, at λ 7 m., have been applied to the calculation of mol. dimensions, using the formula $t=4\pi\eta r^3/kT$ (t=time of relaxation in sec., k=Boltzmann const., η=viscosity, T=abs. temp., r=radius of mol. supposed spherical). For non-spherical mols. r^3 can be replaced by the product of 3 radii along 3 orthogonal axes, one of which is in the same direction as the electric moment, and passing through the centre of gravity of the mol. C. R. H.

Absorption of various alcohols at high frequencies. R. Zouckermann and R. Freymann (Compt. rend., 1936, **202**, 2079—2081).—No narrow bands were observed in the absorption by 7 primary alcohols of waves of 3—12 m. length. In a homologous series with a fixed λ, the conductivity increases rapidly at first, and tends to a const. val. for mols. with $>$ 5 C. H. J. E.

Dipole *ortho*-effect. L. Tiganik (Keem. Teated, 1935, **2**, 88—106; Chem. Zentr., 1935, ii, 2936).—On the view that the *ortho*-effect is due to electron displacements, not to deflexion of valency angles, a theory is developed on classical electrostatic lines, and applied to C_6H_6 and its substitution products. Vals. for dipole moments so calc. agree with experimental vals. It is considered, however, that in C_6H_6, the H atoms are displaced from the plane of the ring. J. S. A.

Electric dipole moments of nitrophenols. H. O. Jenkins (J.C.S., 1936, 1049).—The dipole moment of o-$NO_2 \cdot C_6H_4 \cdot OH$ in C_6H_6 solution at 25° has been redetermined and its relatively low val. confirmed. The moments of substituted phenols are discussed briefly. D. C. J.

Index of refraction of water and paraffin at high frequencies. L. S. Skaggs and R. T. Dufford (Physical Rev., 1935, [ii], **47**, 201—202).—Measurements at λλ of approx. 10 cm. agree with classical electromagnetic theory. L. S. T.

Effect of pressure on the refractive index of carbon disulphide. F. E. Poindexter (Physical Rev., 1935, [ii], **47**, 202).—Vals. of n for CS_2 for each of the Hg lines 5790, 5460, and 4360 A. are recorded for pressures from 1 to 1880 kg. per sq. cm. Dispersion increases over the whole range of pressure, the increase being more rapid at lower pressures. L. S. T.

Influence of dilution on the molecular refractivities of complex cyanides and cobaltammines. A. K. Bhattacharya (J. Indian Chem. Soc., 1936, **13**, 284—293).—The R_L of complex cyanides at 21° and of cobaltammines at 30° were measured at concns. up to 0·1 mol. For the more stable cyanides R_L decreases with dilution, but for the less stable cyanides and for most of the cobaltammines R_L increases with dilution. This latter effect is ascribed to the decomp. of the complex ions into simpler ions. C. R. H.

Utilisation of molecular refraction for determining constitution and configuration of sugars.—See this vol., 1094.

Refractivity of α-chloronitriles. J. Vandewijer (Bull. Soc. chim. Belg., 1936, **45**, 251—269).—The prep., d, and n for the H_α, H_β, H_γ, and D lines at 15° and 30° of the first 10 members of the homologous series commencing $CH_2Cl \cdot CN$ are recorded. The n of the series is minimal at C_3 and a periodicity persists to C_7. From the mol. refractivities at 20°, the sp. refractivity of Cl less that of H is H_α 5·059, D 5·083, H_β 5·155, H_γ 5·201, from which data for H (A., 1934, 132) give the sp. refractivities of Cl H_α 6·086 and D 6·120. J. G. A. G.

Liquids of high refractive index. B. W. Anderson and C. J. Payne (Nature, 1936, **138**, 168).—A correction (cf. A., 1934, 163) and an acknowledgment of priority. L. S. T.

Optical polarisation ellipsoids of the hydrogen halide gases. C. H. D. Clark (Nature, 1936, **138**, 126).—These ellipsoids constitute similar solid figures. The four H halides have equal optical anisotropies and the optical polarisability perpendicular to the internuclear axis of symmetry is approx. 75% of that along this axis. This latter val. is equal to the polarisability of the halogen ion X^-. L. S. T.

Optical rotation of tartaric acid in presence of titanium ion. M. Schenk (Helv. Chim. Acta, 1936, **19**, 639—645).—The val. of [α] of Ti^{IV} tartrate depends on [$H^\cdot$], and shows max. in both acid and alkaline solutions separated by a sharp min. Aq. tartaric acid in presence of Ti^{IV} oxalate (contrary to the sulphate) shows mutarotation during neutralisation with KOH, due to slow hydrolysis of the tartrate. T. G. P.

Rotatory power of methyl tartrate.—See this vol., 1093.

Analysis of rotatory dispersions of configuratively related halides. P. A. Levene, A. Rothen, and R. E. Marker (J. Chem. Physics, 1936, **4**, 442—449).—Rotatory dispersion curves of halides of the type $CHMeR \cdot [CH_2]_n \cdot X$ (X=halogen, R=alkyl) have been analysed in the visible and ultra-violet regions. Changes due to variations of X and R and the val. of n (1—4) are discussed. H. J. E.

Variation with temperature of the magnetic birefringence of nitric oxide and oxygen under pressure. H. Bizette and B. Tsaï (Compt. rend., 1936, **202**, 2143—2145).—Previous work (this vol., 140) has been extended to temp. −80° to 20°. C. R. H.

Old and new chemistry of radicals. P. H. Hermans (Chem. Weekblad, 1936, **33**, 442—450).—A lecture. S. C.

Valency and molecular structure. J. DeVries (J. Chem. Educ., 1936, **13**, 320—324). L. S. T.

Nature of the hydrogen bond. I. Association in carboxylic acids. R. H. Gillette and A. Sherman (J. Amer. Chem. Soc., 1936, **10**, 1135—1139).—Theoretical. The wave function should include polar and homopolar terms. The H linking consists of at least the states $X^-H^+X^-$, X–HX, and XH–X. E. S. H.

Chemical linking. A. E. van Arkel (Chem. Weekblad, 1936, **33**, 454—457).—A lecture dealing principally with the quantum mechanics of simple mols. S. C.

Relations between functions of cohesion forces of liquids and their chemical function at the b.p. under constant pressure. G. Duch (Compt. rend., 1936, **202**, 1977—1979).—Theoretical. H. J. E.

Dissociation energy of diatomic sulphur, selenium, and tellurium vapours. P. Goldfinger, W. Jeunehomme, and B. Rosen (Nature, 1936, **138**, 205—206).—Vals. deduced from spectroscopic and thermochemical data are discussed. L. S. T.

Relation between internuclear distance and group number for diatomic hydrides. H. C. Corben (Phil. Mag., 1936, [vii], **22**, 144—145).—The equilibrium internuclear distance for the ground state (r_e) is related to the no. of electrons outside closed shells (n) by the expression $r_e n = a + bn - c(n-1)^3$, where a and c are consts. and b depends on the mol. period. The following vals. of r_e are predicted: SH 1·362, ScH 1·90, TiH 1·81, VH 1·72, CrH 1·64, MnH 1·55 A. H. J. E.

Distribution of energies of electrons. J. S. E. Townsend (Phil Mag., 1936, [vii], **22**, 145—171). H. J. E.

Nuclear separation of the S_2 molecule by electron diffraction. L. R. Maxwell, V. M. Mosley, and S. B. Hendricks (Physical Rev., 1936, [ii], **50**, 41—45).—The nuclear separation of the S_2 mol. from S_2 vapour at 800° was 1·92±0·03 A. The electron diffraction pattern of the vapour changes considerably at temp. $<$ 800° owing to the formation of S_{2+n} mols. The S–S–S angle in the higher mol. forms is about 100°, and the S–S distance between neighbouring atoms, 2·1 A. These vals. are in agreement with those found by Warren *et al.* (A., 1935, 285) for the symmetrical puckered S_8 ring in the rhombic form. A. J. M.

Atomic forces of solid states, I, II. W. Wen-Po (Phil. Mag., 1936, [vii], **22**, 49—68).—Theoretical. A method of calculating at. radii and thermal expansion is described. H. J. E.

Ground state vibrational frequencies. H. G. Howell (Nature, 1936, **138**, 36).—The arithmetic mean of the vibrational frequencies of two mols. A_2 and B_2 belonging to the same periodic group approx. equals the frequency of the mol. AB. PN and AsN do not conform to this rule. L. S. T.

Determination of van der Waals forces. H. S. W. Massey and R. A. Buckingham (Nature, 1936, **138**, 77).—Vals. of the van der Waals energy const. C calc. from data (A., 1935, 1295) on the collision of rare gas with alkali atoms agree with those derived from the polarisabilities of the atoms, suggesting that the free path method serves for the determination of these forces. L. S. T.

Van der Waals potential and the lattice energy of a n-CH_2 chain molecule in a paraffin crystal. A. Müller (Proc. Roy. Soc., 1936, **A**, **154**, 624—639).—The van der Waals potential of a CH_2 group in a paraffin crystal is calc. by applying London's theory (A., 1930, 525). The mol. must be subdivided for the purpose of calculation, but it is found that for different modes of subdivision the final val. of the potential is the same. L. L. B.

Molecular energy of alkali halides. E. J. W. Verwey and J. H. de Boer (Rec. trav. chim., 1936, **55**, 431—443).—More correct vals. of the lattice and mol. energies (cf. A., 1932, 564) have been calc., which give the following vals. of the electron affinity: F′ 92·2, Cl′ 83·0, Br′ 77·2, and I′ 69·9 kg.-cal. Mol. energy vals. for the alkali halide vapours are calc. for different mol. models, and the effect of the polarisation forces is also considered. The mols. of the alkali halides are perfect ionic mols. O. J. W.

Energy and structure of the molecules of the alkaline-earth oxides. J. H. de Boer and E. J. W. Verwey (Rec. trav. chim., 1936, **55**, 443—450; cf. preceding abstract).—The lattice energies of BeO, MgO, CaO, SrO, and BaO have been calc. The calc. val. of the electron affinity of O ($O \rightarrow O''$) is −173 kg.-cal. The vals. of the mol. energy calc. for these mols. are considerably $<$ those derived from the lattice and sublimation energies. It is probable that the vapours of these oxides, which have ionic lattices in the solid state, consist mainly of homopolar mols. O. J. W.

Physical chemistry of homologous series. E. M. Bruins (Rec. trav. chim., 1936, **55**, 419—420).—Formulæ are derived for the electrostatic potential in a homologous series surrounding a single charge and a dipole. O. J. W.

Determination of linking moments in polyatomic molecules. R. Mecke (Z. physikal. Chem., 1936, **B**, **33**, 156—162).—Theoretical. The previously described method (this vol., 268) of calculating for characteristic valency vibrations, where the energy is largely localised in a linking, the linking moment, μ, from the intensities of the overtones has been simplified. By plotting the transition moments derived from the total absorption of the individual bands against v and extrapolating to $v=0$ μ is obtained. An examination of the conditions for this extrapolation indicates that it would be possible to derive abs. partial dipole moments from suitable absorption measurements. R. C.

Characteristic periods of vibrations of ionised gases in a magnetic field. T. V. Ionescu (Compt. rend., 1936, **203**, 57—59).—Mathematical. C. R. H.

Electron affinity of free radicals. X. Potentiometric method for determining ΔF for the addition of sodium to an organic compound. H. E. Bent and N. B. Keevil (J. Amer. Chem. Soc., 1936, **58**, 1228—1233; A., 1935, 1188).—Apparatus and procedure are described. Didiphenylenediphenylethane has an abnormally high electron affinity, which is related to the strength of phenylfluorene as an acid. E. S. H.

Collisions of the second kind and electron affinity. L. Goldstein (Compt. rend., 1936, **202**, 2057—2059; cf. this vol., 656).—Negative ions cannot be produced directly in pure O_2, SF_6, or CF_4. In presence of 1% of A, Kr, or Xe, metastable atoms of the rare gas are produced by electronic collisions, and these dissociate O_2, SF_6, or CF_4 by collisions of the second kind. The resulting electronegative atoms can form negative ions. H. J. E.

Functional space in quantum mechanics. L. Chadenson (Compt. rend., 1936, **202**, 1974—1977). H. J. E.

Some lattice sums involved in the calculation of elastic constants. M. Goeppert-Mayer and A. May (Physical Rev., 1936, [ii], **50**, 99).—The method of calculation of the electrostatic part of the consts. C_{11} and C_{12} for crystals of the CsCl type is given. A. J. M.

Rotation of dipole molecules in solid bodies. J. Frenkel (Acta Physicochim. U.R.S.S., 1935, **3**, 23—36).—Fowler's theory of the rotation of mols. in solids (A., 1935, 683) is compared with the Pauli method of determining the orientation of mols. in a polar gas on application of an external field. The theory is extended to the case where the orienting field acting on any given mol. of the crystal depends on the neighbouring mols. and has not a const. val. An expression is obtained for the transition temp. of a solid, this expression being similar to that for the Curie temp. of a ferromagnetic solid. A. J. M.

Surface tension of mercury in presence of gases. I. Dry air. M. Kernaghan (Physical Rev., 1935, [ii], **47**, 202; cf. A., 1931, 788).—γ falls rapidly from 464 dynes per cm. in a vac. until an apparently crit. pressure of 7 mm. of dry air is reached. At higher pressures γ remains approx. const. L. S. T.

(A) Increments of parachor of polymethylenic rings. (B) Multiple linkings in molecules of carbon compounds, and the structural constants of molecular refraction. V. S. Gutiria (J. Gen. Chem. Russ., 1936, **6**, 340—349, 455—459).—(A) Experimental vals. of increments in parachors of homologous series of cyclic polymethylenic hydrocarbons differ considerably from those calc. from Mumford and Phillips' formulæ (A., 1929, 1219), or from other formulæ derived by Gutiria.

(B) The structural consts. of mol. refraction, *MR*, of C·C, C:C, and C⋮C compounds are derived from $K=am \sin \alpha + b$, where m represents the no. of linkings between C atoms, α is the angle subtended by the lines of valency, and a and b are consts., depending on the λ of the light used. The vals. calc. for *MR* are in satisfactory agreement with those calc. by the usual formula, and with experiment, for a no. of hydrocarbons. R. T.

Temperature function of *X*-ray reflexion in the neighbourhood of the m.p. of a crystal. R. B. Jacobs and A. Goetz (Physical Rev., 1935, [ii], **47**, 94—95).—Deviations from the Debye–Waller function near the m.p. of Bi crystals are described. L. S. T.

Effect of temperature on the reflexion of *X*-rays by crystals. III. High temperatures. Allotropic crystals. C. Zener and S. Bilinsky (Physical Rev., 1936, [ii], **50**, 101—104; cf. this vol., 273).—The former discrepancy at high temp. disappears when account is taken of the variation of the characteristic temp. with temp. A relationship is found between the temp. factors for two allotropic forms of the same element. N. M. B.

Absolute atomic factors of sulphur and lead. P. de la Cierva and J. Palacios (Anal. Fís. Quím., 1935, **33**, 34—38).—The intensity of the (220) reflexion of PbS has been compared with that of the (200) reflexion of NaCl, whence from the data of James *et al.* (A., 1928, 225) the val. of the *F* factor for PbS is 63·15 for sin $\theta/2=0{\cdot}238$, which, combined with the authors' curves (A, 1935, 908) for Pb and S, gives the abs. curves of the *F* factors. F. R. G.

New and unexplained effects in Laue *X*-ray reflexion in calcite. J. W. M. DuMond and V. L. Bollman (Physical Rev., 1936, [ii], **50**, 97).—Incomplete blackening was observed where complete blackening of the plate would be expected in the Laue *X*-ray reflexion through thin cleaved plates of calcite. It was found that emergent beams which should be parallel were slightly convergent. Along the lengths of paired spectral lines there were marked fluctuations of intensity not due to interference. A. J. M.

Mathematical modulus derived from *X*-ray data for evaluation of residual distortion in crystals. G. L. Clark and M. M. Beckwith (Physical Rev., 1935, [ii], **47**, 200; cf. A., 1935, 1193). L. S. T.

Scattering of *X*-rays by gases. E. O. Wollan (Physical Rev., 1935, [ii], **47**, 201). L. S. T.

Diffuse scattering of *X*-rays by crystals. G. E. M. Jauncey (Physical Rev., 1935, [ii], **47**, 201). L. S. T.

Recrystallisation and crystal growth in aluminium. A. von Zeerleder (Schweiz. Arch. angew. Wiss. Tech., 1935, **1**, 148—151; Chem. Zentr., 1935, ii, 2873).—Crystal growth in deformed Al at 550° is discussed. J. S. A.

Crystallisation of supercooled dielectric liquids in an electric field. R. Swinne (Wiss. Veröff. Siemens-Werken, 1936, **15**, 124—128).—Polar substances ($PhNO_2$, fenchone, and PhCN) were crystallised from the supercooled liquids with and without the application of an electric field (up to 5 kv. per cm.). Without a field, crystals did not usually appear between the electrodes, but when the field was applied crystallisation between them was more marked than elsewhere. With non-polar substances (C_6H_6) the field caused no difference in the crystallisation. A. J. M.

Structure of radicals in crystals. W. H. Zachariasen (Physical Rev., 1935, [ii], **47**, 201). L. S. T.

Nature of viscid fluid threads. (Sir) J. Larmor (Nature, 1936, **138**, 74). L. S. T.

Orientation of molecules on the surface of solids and liquids. F. Kőrösi (Tech. Kurir, 1936, **7**, No. 7, 2—4).—A review. E. P.

Crystal structure of carbon. U. Hofmann and D. Wilm [with E. Csalán] (Z. Elektrochem., 1936, **42**, 504—522).—*X*-Ray determinations for coarsely-cryst. graphite give *a* 4·252, *c* 6·69 A. As the crystal size diminishes, lattice distortion appears, reaching a max. in active C. There is a continuous gradation of structure from graphite to active C; distortion is already detectable in Ceylon and Acheson graphite. Crystal growth begins at 1400°. The alteration of the structure by oxidation has been studied. E. S. H.

Composition and crystal structure of trigonal chromium and manganese carbides. A. Westgren (Jernkont. Ann., 1935, **118**, 231—240).—The cell dimensions are: Cr carbide, *a* 13·98, *c* 4·523 A.; Mn carbide *a* 13·87, *c* 4·53 A. On rotation photographs of the latter about the axis (001) the only prism reflexions (*hko*) visible are those with *h* and *k* even. The no. of atoms in the unit cell must be a multiple of 4. The formula Mn_7C_3 (80 atoms per unit cell) is supported. Ch. Abs. (*e*)

Structure of potassium tetroxide. V. Kassatochkin and V. Kotov (J. Chem. Physics, 1936, **4**, 458).—KO_2 forms a tetragonal face-centred lattice of the CaC_2 type (*a* 5·70, *c* 6·72 A.; 4 mols. in unit cell; space-group $D_{4h}^{17}-F4/mmm$). The distance between adjacent O nuclei is 1·28±0·07 A. The formula KO_2 is supported. H. J. E.

Fourier analysis of *X*-ray patterns of vitreous SiO_2 and B_2O_3. B. E. Warren, H. Krutter, and O. Morningstar (J. Amer. Ceram. Soc., 1936, **19**, 202—206).—Analysis of the patterns obtained in vac. with monochromatic Mo and Cu radiations showed that SiO_2 is a tetrahedral Si–O network and that B_2O_3 is a triangular co-ordination of B atoms surrounded by shared O atoms. The results agree with the Zachariasen prediction of the structure of oxide glasses. The glass-forming tendency of these two oxides is due to the complex irregular aggregate structures which require much rearrangement during cooling to assume a symmetrical (cryst.) structure and to the flexibility (*i.e.*, stability) of the linking between an O and two cations. J. A. S.

Crystal structure and colloid-chemical properties of vanadium pentoxide. J. A. A. Ketelaar (Natuurwetensch. Tijds., 1936, **18**, 80).—A brief discussion (cf. this vol., 274). D. R. D.

Cation arrangement in a few oxides with crystal structures of the spinel type. E. J. W. Verwey and J. H. de Boer (Rec. trav. chim., 1936, **55**, 531—540).—The electrical conductivity of Fe_3O_4, with a cubic spinel lattice, is 10^8 times that of Mn_3O_4 and Co_3O_4 with a closely related tetragonal lattice. This difference is to be explained by differences in the valency state of the cations, and in the arrangement of the cations among the lattice points of the spinel unit cell. The high conductivity of Fe_3O_4 may be explained on the conception that the oxide is FeO,Fe_2O_3. The crystal contains equal amounts of Fe^{++} and Fe^{+++} in the equiv. lattice points. The low conductivity of Co_3O_4 together with considerations of energy, and study of *X*-ray structure, leads to the conclusion that it is made up of Co^{++} and Co^{++++}. Mn_3O_4 has a structure similar to Co_3O_4, but the cell is distorted tetragonally. Both Mn_3O_4 and Co_3O_4 are true spinels. The *X*-ray diagram of γ-Fe_2O_3, having crystal structure closely related to spinel, shows that there are a no. of vacant cationic positions. The Mn_2O_3,H_2O obtained by Dubois (A., 1935, 181, 946) may be regarded as γ-Mn_2O_3. It has a face-centred tetragonal cell, similar to the γ-Fe_2O_3 cell, but distorted. A. J. M.

Structure of metal hydroxides with the emanating power 1·00. O. Erbacher (Z. physikal. Chem., 1936, **B**, **33**, 47—53).—$Fe(OH)_3$ preps. of this type (cf. A., 1926, 332) give an amorphous *X*-ray diagram. Their radioactive emanating power shows them to have an exceptionally open internal structure. R. C.

Morphology of pigments. III. *X*-Ray study of litharge. E. G. Ivantscheva (J. Gen. Chem. Russ., 1936, **6**, 621—625).—PbO prepared by the Barton process crystallises in the rhombic system, whilst oven PbO consists of tetragonal crystals. Pb_2O_3 gives a characteristic *X*-ray spectrum, indicating that it is not a mixture of PbO and PbO_2. R. T.

Structure of silver azide. M. Bassière (Bull. Soc. franç. Min., 1935, **58**, 333—340; cf. this vol., 16). L. S. T.

Monohydrated sulphates of the magnesium series. F. Hammel (Compt. rend., 1936, **202**, 2147—2149).—The dimensions of the unit cells of monohydrated Mg, Mn, Fe, Co, Ni, Cu, and Zn sulphates have been calc. (cf. this vol., 413). C. R. H.

Calcium sulphate hemihydrate and the anhydrites. I. Crystallography. W. A. Caspari (Proc. Roy. Soc., 1936, **A**, **155**, 41—48).—The prep., properties, and morphology of single crystals of $CaSO_4,0{\cdot}5H_2O$ (I) are described. *X*-Ray analysis gives the probable space-group as D_{3d}^1 or D_{3d}^3, 3 mols. per unit cell, *d* 2·60. The arrangement of ions in the lattice is discussed. The suggested structure leaves channels between Ca^{++} and SO_4^{--} ions, along which H_2O mols. can circulate. Dehydration of (I) under conditions short of conversion into anhydrite (II) causes slight mechanical changes in the crystal, but leaves the lattice unaltered. From the fact that the dihydrate and (I) yield the same substance under these conditions, it is concluded that there is only one crystal species intermediate between (II) and dihydrate. Sol. (I) has crystals belonging to the trigonal system, *a* 6·82, *c* 6·24 A., *d* 2·70. L. L. B.

Crystalline form and optical properties of calcium iodate. J. Mélon (Bull. Soc. franç. Min., 1935, **58**, 343—349).—$Ca(IO_4)_2,6H_2O$ is not truly dimorphous. Crystals obtained in presence of HNO_3 and of $CaCrO_4$ show only facial differences. n_g 1·686, n 1·644, and n_p 1·604. L. S. T.

Crystallography of cæsium molybdotellurates. J. D. H. Donnay and J. Mélon (Amer. Min., 1936, **21**, 299—311).—Cs molybdotellurate crystallises in two types, (i) equant, biaxial positive, and (ii) tabular, biaxial negative, both being triclinic and apparently holohedral. (i) has $a:b:c=0{\cdot}9498:1:0{\cdot}6059$, α 96° 41′, β 102° 1′, γ 101° 31′, n_α 1·709, n_β 1·716, n_γ 1·797. (ii) has $a:b:c=0{\cdot}9365:1:0{\cdot}7989$, α 93° 45′, β 94° 8′, γ 88° 21′, n_α 1·669, n_β 1·734, n_γ 1·738. L. S. T.

Crystal structure of metaldehyde. L. Pauling and D. C. Carpenter (J. Amer. Chem. Soc., 1936, **58**,

1274—1278).—*X*-Ray data indicate a body-centred unit, having a_0 10·40, c_0 4·11 A., containing two mols. of $(MeCHO)_4$. The space-group is C_4^5—I_4; parameter vals. have been determined. The mol. consists of an 8-membered –O–C–O–C– ring with H and Me attached to each C. The interat. distances and linking angles are the same as in $(MeCHO)_3$.
E. S. H.

Crystallographic study of tartaric acid derivatives. J. WYART and Y. KI-HENG (Compt. rend., 1936, **203**, 95—97).—The vals. of *a*, *b*, and *c*, respectively for the following compounds are: tartramide, 10·0, 12·2, 4·90; tartramic acid 12·30, 7·96, 6·00; Me tartrate, 18·50, 10·00, 8·45; K borotartrate, 4·88, 18·00, 7·65 A. C. R. H.

Diffraction of *X*-rays by the higher polyethylene glycols and by polymerised ethylene oxides. W. H. BARNES and S. ROSS (J. Amer. Chem. Soc., 1936, **58**, 1129—1131).—The *X*-ray diagrams show no essential difference between the higher polyethylene glycols and polymerised ethylene oxides. E. S. H.

Change of lattice of fibroin when completely dried in a vacuum. V. MATSUNAGA (Naturwiss., 1936, **24**, 446—447).—The lattice const. of ordinary fibroin (containing some H_2O) is the same as that of the substance which has taken up as much H_2O as possible, and > that of completely dried fibroin.
A. J. M.

***X*-Ray analysis of keratins.**—See this vol., 1138.

Crystal orientation in tooth-enamel.—See this vol., 1010, 1011.

Formation and crystallisation of vitreous media. W. T. RICHARDS (J. Chem. Physics, 1936, **4**, 449—457).—A discussion. It is shown to be unnecessary to postulate a vitreous state of aggregation, since all the properties of glasses appear to be those of undercooled liquids of high η. H. J. E.

Electron-optical reproduction with electrons liberated photo-electrically. H. MAHL and J. POHL (Z. tech. Phys., 1935, **16**, 219—221; Chem. Zentr., 1935, ii, 2626; cf. A., 1935, 139). J. S. A.

Kikuchi lines from etched copper crystal. W. COCHRANE (Nature, 1936, **138**, 202—203).—An etched single crystal of Cu, protected from distortion, gives Kikuchi lines, in addition to the cross-grating pattern of spots, by diffraction of a fast electron beam. These lines form a criterion of perfection of the crystal lattice. L. S. T.

Oxide layer on a polished copper surface. S. DOBINSKI (Nature, 1936, **138**, 31).—The electron diffraction pattern usually attributed to polished Cu is due to Cu_2O. Polishing in absence of air gives haloes of different size corresponding with spacings of 1·91 and 1·16 A. L. S. T.

Anomalous values of lattice spacings obtained by electron diffraction. E. PICKUP (Nature, 1936, **137**, 1072).—Attention is directed to discrepancies in lattice spacings calc. from electron diffraction patterns. These anomalies may invalidate the results of electron-wave methods for measuring at. consts. L. S. T.

Analytic method of interpretation of electron diffraction photographs of gases. S. H. BAUER (J. Chem. Physics, 1936, **4**, 406—412).—A simplified method of calculating interat. distances and valency angles is described. Published data for CH_2Cl_2, $CHCl_3$, and $COCl_2$ are recalc. and modified. New measurements on C_3H_8 are recorded. H. J. E.

Electron-diffraction study of paraldehyde. D. C. CARPENTER and L. O. BROCKWAY (J. Amer. Chem. Soc., 1936, **58**, 1270—1273).—$(MeCHO)_3$ consists of a staggered, 6-membered ring of alternate C and O atoms, having a C–O distance of 1·43±0·02 A. The linking angles are tetrahedral and the Me groups are placed symmetrically about the mol. in nearly the same plane as the ring, with the possibility that only one Me may be above the plane of the ring. The C of the Me groups are attached to the C of the ring by linkings having a length of 1·54±0·02 A. E. S. H.

Study of the nature of liquids by means of *X*-ray diffraction. G. W. STEWART (Physical Rev., 1935, [ii], **47**, 201). L. S. T.

Theory of the piezo-resistive effect. J. W. COOKSON (Physical Rev., 1935, [ii], **47**, 194—195).—The change in electrical resistance which a homogeneous body undergoes when subjected to mechanical stress is discussed for a Bi crystal. L. S. T.

Dependence of dielectric properties of Seignette salt crystals on mechanical factors. R. DAVID (Helv. phys. Acta, 1935, **8**, 431—484; Chem. Zentr., 1935, ii, 3207—3208).—The effect of pressure on the hysteresis and polarisation phenomena was studied.
H. J. E.

Magnetic properties of manganese heated in nitrogen. L. F. BATES, R. E. GIBBS, and D. V. REDDI-PANTULU (Proc. Physical Soc., 1936, **48**, 665—671).—The combination of amorphous Mn with N_2 has been studied between 300° and 1000°. Ferromagnetic compounds are formed at temp. much < previously reported. The magnetic hysteresis phenomena, the ferromagnetic Curie points, and an *X*-ray study of the compounds are described. The ferromagnetism can be associated with the γ-phase of Mn with a slightly enlarged lattice const.; the function of the N_2 is not understood. W. R. A.

Ferromagnetism of nickel. II. Temperature effects. J. C. SLATER (Physical Rev., 1936, [ii], **49**, 931—937; cf. this vol., 671).—With the help of Fermi statistics and the model previously proposed, the free energy is calc. as a function of temp. and magnetic moment. The val. of the latter for which the free energy is a min. decreases with rise of temp. to zero at the Curie point, and, with the free energy val. at the min., as a function of temp., agrees with experiment. At abs. zero not all the spins are parallel, and this effect probably becomes more pronounced on approaching Fe in the ferromagnetic series, explaining the fact that alloys of Fe and Co show the highest saturation moments, the moment decreasing in Fe and in its alloys with lighter elements.
N. M. B.

Magnetisation of nickel under compressive stresses and the production of magnetic dis-

continuities. C. W. Heaps (Physical Rev., 1936, [ii], **50**, 176—179).—Hysteresis curves for stresses up to the elastic limit have been obtained. The existence of contiguous compressed and stretched regions appears necessary for the production of large Barkhausen discontinuities. N. M. B.

Behaviour of some solidified gases in polarised light. E. Pohland (Angew. Chem., 1936, **49**, 482—483).—Optical examination in polarised light between crossed nicols shows that solid HCN, NO, and SO_2 are double refracting, and that SbH_3 is dimorphous, the cubic form being the stable one. J. W. S.

Cryolite. Index of refraction, birefringence, and crystalline forms. G. Cesàro and J. Mélon (Bull. Acad. roy. Belg., 1936, [v], **22**, 362—372).—n for cryolite is 1·343 at 6620 A. and 1·319 at 4770 A. The vals. obtained at other λλ agree with those calc. from the Cauchy formula ($n=A+B/\lambda^2$). The birefringence for various faces, and the angles between the faces, are calc. A. J. M.

Allotropy of very pure calcium. A. Schulze (Z. Metallk., 1936, **28**, 55—57).—The ordinary face-centred cubic (α) form of Ca is converted into a body-centred (β) form at 300° and into a close-packed hexagonal (γ) form at 450°. The β–γ change is accompanied by a heat evolution of 5·3 g.-cal per g. These results have been established by thermal, dilatometric, X-ray, and electrical resistance methods. A. R. P.

Highly polymerised compounds. CXLI. Osmotic mol. wt. determinations with polymer-homologous series of substances of high mol. wt. G. V. Schulz (Z. physikal. Chem., 1936, **176**, 317—337).—Mol. wts. of cellulose nitrates, polyethylene oxides, and polystyrenes have been deduced from osmotic pressure measurements by means of the equation previously suggested (this vol., 146). Mol. wts. up to 10^6 may be determined by this method. A convenient osmometer is described. R. C.

α–β Transition with mechanically treated and with untreated zirconium. J. H. de Boer, P. Clausing, and J. D. Fast (Rec. trav. chim., 1936, **55**, 450—458).—Measurements of the electrical resistance of Zr rods, which had been subjected to varying preliminary treatment, show that the indefinite character of the α→β transition is not due to the transition itself, but to the heating of the rods in air during the mechanical working. The α→β transition temp. is 865±10° (cf. A., 1932, 219). O. J. W.

Influence of oxygen and nitrogen on the α–β transition of zirconium. J. H. de Boer and J. D. Fast (Rec. trav. chim., 1936, **55**, 459—467; cf. preceding abstract).—Zr can take up homogeneously $\not<$ 10 at.-% of O and of N, and in presence of these gases the α–β transition is no longer sharp, but extends over a temp. range. With 10 at.-% O the transition commences below 910° and extends to >1550°. In this temp. range the β-phase is in equilibrium with an α-phase which is richer in O. The resistance curves are scarcely influenced by the addition of Al. O. J. W.

High-temperature properties of niobium. A. L. Reimann and C. K. Grant (Phil. Mag., 1936, [vii], **22**, 34—38).—Measurements of the sp. resistance, total thermal radiation, electron emission, and rate of evaporation at 1800—2400° abs. are recorded. The m.p. was 2770° abs. H. J. E.

Electrical resistivity of bismuth single crystals. A. B. Focke and J. R. Hill (Physical Rev., 1936, [ii], **50**, 179—184).—Measurements in the temp. range −185° to 100° on Bi crystals containing Pb, Sn, Sb, or Te showed, in general, that falling temp. results in greater effectiveness of the impurity except when the impurity concn. allows phase separation at low temp. Less than 0·03% of all impurities cause a sharp increase in the resistance. The effect of larger amounts depends on the nature of the impurity; Pb and Sn increase the resistance; Te lowers it below the val. for pure Bi; Sb causes the initial rise to fall off and then to be slowly re-established; >0·03% Sn and >0·2% Pb result in a negative temp. coeff. for resistance parallel to the principal axis. N. M. B.

Electrical resistance of bismuth alloys. N. Thompson (Proc. Roy. Soc., 1936, **A**, **155**, 111—123).—The electrical resistance of single crystals of Bi containing traces of Pb, Sn, Ge, Se, Te, and other elements has been measured from 14° to 400° abs. Pb, Sn, and Ge dissolves in the Bi lattice, giving an alloy with a high negative temp. coeff. of resistance parallel to the principal axis of the crystal, and a similar, but smaller, effect perpendicular to the axis. Se and Te dissolve in Bi, but there is no negative temp. coeff.; the addition of the first trace of the impurity lowers the sp. resistance, both parallel and perpendicular to the axis, except at low temp. The results are discussed in the light of Jones' theory of Bi (A., 1935, 153). L. L. B.

Time effects in superconductors. K. Mendelssohn and R. B. Pontius (Nature, 1936, **138**, 29—30). L. S. T.

Carrier electrons in superconduction. R. Forrer (Compt. rend., 1936, **202**, 2059—2061).—The electrons which are responsible for superconduction are the *s* electrons of incomplete shells. H. J. E.

Electrostatic behaviour of superconductors. H. London (Proc. Roy. Soc., 1936, **A**, **155**, 102—110; cf. A., 1935, 689).—It follows from measurements of the capacity of a superconducting condenser that no electrostatic fields exist in a pure superconductor, and that in all stationary cases the surface of a superconductor is equipotential. L. L. B.

Conductivity of *p*-azoxyanisole. M. Jeżewski and M. Miesowicz (Acta phys. polon., 1934, **3**, 279—283; Chem. Zentr., 1935, ii, 5052).—Conductivity data are recorded at 121° for d.c. and a.c., and with longitudinal and transverse magnetic fields of 4000 gauss. H. J. E.

Magnetic measurements in chemistry. J. S. Anderson (Chem. and Ind., 1936, 555—559).—The application of magnetic susceptibility measurements to chemical problems is reviewed. J. S. A.

Collective electron specific heat and spin paramagnetism in metals. E. C. Stoner (Proc. Roy. Soc., 1936, **A**, **154**, 656—678).—General expressions are obtained which show how the sp. heat and spin paramagnetism, and their temp. variation, depend on the band form. Only the low temp. range is considered. A method of determining the effect of interchange interaction is developed. Positive interchange interaction does not necessarily result in ferromagnetism, even at the lowest temp. The magnetic properties of the elements of the first two columns of the periodic table and of the transition elements and rare earths are considered on the basis of the theoretical treatment. L. L. B.

Magnetic properties of the plasma of gas discharges. M. Steenbeck (Wiss. Veröff. Siemens-Werken, 1936, **15**, 1—17).—The plasma of a gas discharge may be treated as a metal with freely moving, non-degenerate electron gas. The diamagnetic susceptibility and magnetic moment induced in the plasma are determined. The susceptibility is > that of any other diamagnetic substance. A. J. M.

Preparation of lithium alum. J. F. Spencer and G. T. Oddie (Nature, 1936, **138**, 169).—Concn. and cooling in an ice–NaCl freezing mixture of an aq. solution of Li_2SO_4,H_2O and $Al_2(SO_4)_3,18H_2O$ (1 : 1) yields isotropic crystals, a combination of cube and octahedron, of Li alum. At room temp. the crystals decompose; at 200°, all H_2O is lost and a bulky, friable mass remains. The mass susceptibility is $-0{\cdot}541\times10^{-6}$. L. S. T.

Magne-crystallic action. IV. Magnetic behaviour of paramagnetic ions in the *S*-state in crystals. K. S. Krishnan and S. Banerjee (Phil Trans., 1936, **A**, **235**, 343—366; cf. A., 1935, 924).—Special technique for the measurement of feeble anisotropies, and data for 10 paramagnetic single crystals of Mn^{++} and Fe^{+++} salts, 13 isomorphous diamagnetic crystals obtained by replacing Mn by Mg or Zn, and Fe by Al, and abs. susceptibilities of the 10 first-mentioned are given. Causes discussed contributing to the anisotropy are: diamagnetism of the crystal, mutual influence of the magnetic moments and their non-cubic arrangement in the crystal lattice, and the Stark splitting of the ^6S levels under the influence of the cryst. electric fields. A method for calculating the magnitude of the Stark separation from the anisotropy and the "characteristic temp." is described. The part played by Stark splitting in various low-temp. phenomena is reviewed; the entropy–temp. and sp. heat–temp. curves of the crystals around 0·1° abs. can be predicted from magnetic measurements at room temp. Data for some mixed crystals are given. N. M. B.

Optical method for the measurement of paramagnetic susceptibilities. Application to the ethyl sulphates of the rare earths in the direction of the optic axis. J. Becquerel (Physica, 1936, **3**, 705—723; cf. Van Vleck and Hebb, A., 1934, 944).—Vals. of the magnetic susceptibilities of the hydrated Et sulphates of Pr, Nd, Ds, and Er parallel to the optic axis are deduced from measurements of the magnetic rotatory power at temp. between 1·45° abs. and room temp. Those for Ds are in agreement with direct measurements and all are compatible with the theory of paramagnetism.

O. D. S.

Magnetic properties of some compounds of the rare elements. S. Velayos (Anal. Fís. Quím., 1935, **33**, 5—33; cf. A., 1934, 586).—χ for Er_2O_3, Dy_2O_3, Gd_2O_3, $Gd_2(SO_4)_3$, Pr_2O_3, and Nd_2O_3 has been measured over the range 80—720° abs., whence the magneton nos. are 52·0, 46·8, 38·97, 39·1, 17·5, and 16·4. Pr_2O_3 and Nd_2O_3 do not obey the Weiss–Curie law but obey the modification proposed by Cabrera *et al.* (A., 1925, ii, 755), $(\chi+k)(T+\Delta)=C$. The magneton nos. of Pr_2O_3 and Nd_2O_3 agree more closely with the theoretical vals. of Hund than those of Van Vleck and Frank. F. R. G.

Critical examination of Pascal's value for the magnetic susceptibility of the CH_2 group. S. S. Bhatnagar and N. G. Mitra (J. Indian Chem. Soc., 1936, **13**, 329—334).—Recalculation of Pascal's val. for χ of the CH_2 group, using modern vals. for at. wts. and correcting for the new val. for H_2O, gives, as an average of 50 vals., $-11{\cdot}68\times10^{-6}$ (cf. Pascal's val. $-12{\cdot}35\times10^{-6}$). C. R. H.

Search for a photomagnetic effect. R. M. Emberson and R. T. Dufford (Physical Rev., 1935, [ii], **47**, 202).—Measurements of the magnetic susceptibilities of >60 substances, including Grignard solutions giving the photovoltaic effect, failed to reveal a change in susceptibility due to illumination.

L. S. T.

Dispersion of sound in oxygen. L. S. Sinness and W. E. Roseveare (J. Chem. Physics, 1936, **4**, 427—431).—The velocity of a 1000-cycle sound wave in O_2 of various degrees of humidity at 26·5° was measured. The velocity was a min. for $p_{H_2O}=$ 1—3 mm. The change in velocity due to dispersion was 0·16%. The H_2O mols. are effective in bringing the heat capacity of the first vibrational state of O_2 into equilibrium with the sound wave. H. J. E.

Acoustic experiments for the investigation of molecular collisions. H. O. Kneser (Sitzungsber. Ges. Naturwiss. Marburg, 1935, **69**, 189—194; Chem. Zentr., 1935, ii, 3213).—The absorption of sound waves by air or O_2 is small for high or low frequencies, and is a max. for moderate frequencies. Addition of 1% of H_2 at EtOH increases the absorption considerably. N_2, CO, or He does not change it.

H. J. E.

Molecular absorption of sound in gases. H. O. Kneser (Z. tech. Phys., 1935, **16**, 213—219; Chem. Zentr., 1935, ii, 3213; cf. preceding abstract). —Measurements with air, O_2, and CO_2 agree with the theory of mol. absorption. Foreign gases increase the absorption coeff. H. J. E.

Direct calorimetric determination of C_v of the hydrogen isotope in the solid and liquid state. E. Bartholomé and A. Eucken (Z. Elektrochem., 1936, **42**, 547—551).—Apparatus and technique are described and results reported for solid H_2 (11·20—17·75° abs.), solid D_2 (11·60—21·23° abs.), liquid H_2 (15·33—23·13° abs.), and liquid D_2 (19·62—23·49° abs.). The determinations of C_v

are discussed. Vals. of θ are 105 for H_2 and 97 for D_2. E. S. H.

Specific heat, entropy, and dissociation of technical gases and vapours. E. Justi and H. Lüder (Forsch. Ingenieur. Ausg., 1935, 6, A, 209—216; Chem. Zentr., 1935, ii, 2789—2790).—Data given previously (A., 1935, 289) are supplemented by data for H_2, D_2, N_2, O_2, HD, OH, CO, NO, H_2O, D_2O, CO_2, SO_2, CH_4, C_2H_4, C_2H_2, and air. The variations of C_v and C_p with pressure are discussed, and data are given for the dissociation of H_2, N_2, O_2, NO, H_2O, CO_2, N_2O, SO_2, C_2H_6, and for the water-gas reactions. J. S. A.

Mean specific heats of gases, for use in fuel technical calculations. W. Gumz (Feuerungstech., 1935, 23, 85—86; Chem. Zentr., 1935, ii, 2789).—Mean sp. heats between 0° and 3500° are given for CO_2, SO_2, H_2O, N_2, O_2, A, CO, CH_4, H_2, and air. J. S. A.

Entropy of water and the third law of thermodynamics. Heat capacity of ice from 15° to 273° abs. W. F. Giauque and J. W. Stout (J. Amer. Chem. Soc., 1936, 58, 1144—1150).—The discrepancy between the spectroscopic val. of the entropy and the $\int_0^T C_p d \log T$ for H_2O has been evaluated as 0·82 g.-cal./degree/mol. Heat capacity data for ice are recorded. No difference in thermal properties was observed whether the ice was cooled slowly or rapidly to low temp. or kept for a long time at low temp. E. S. H.

Specific heat of nickel. E. C. Stoner (Phil. Mag., 1936, [vii], 22, 81—106).—An analysis of the sp. heat of Ni is made in terms of the lattice vibration term, the dilatation term, and the electronic and magnetic sp. heats. H. J. E.

Electronic specific heat in palladium. G. L. Pickard (Nature, 1936, 138, 123).—Determinations of the sp. heat of Pd between 2·5° and 22° abs. give $C=0{\cdot}0000224T^3+0{\cdot}0031T$ g.-cal. per degree for the at. heat. The first term represents the component due to the lattice vibrations, and the second the sp. heat of the free electrons or positive holes (unfilled quantum states). As predicted by Mott, the val. of the electronic sp. heat is > that for normal metals and is even > that of Ni. L. S. T.

Exact determination of specific heats at high temperatures. VIII. Additive law for the atomic heats of metals in their binary compounds. F. M. Jaeger and T. J. Poppema (Rec. trav. chim., 1936, 55, 492—517; cf. A., 1934, 354).—Further measurements of C_p for Sb and Pd and for the binary compounds $MgZn_2$, $PtSb_2$, PdSb, $PdSb_2$, Pd_3Sb, PdCu, and $PdCu_3$ are recorded. The observed mol. heat differs in general from that calc. from the component at. heats, and the differences increase with the temp. Some *X*-ray data for β-Pd_3Sb are given. O. J. W.

Specific heats of solid substances at high temperatures. XI. Specific heats, electrical resistance, and thermo-electric behaviour of titanium in their dependence on temperature. F. M. Jaeger, E. Rosenbohm, and R. Fonteyne (Rec. trav. chim., 1936, 55, 615—654).—Ti exists in an α-form with hexagonal symmetry, stable below ~905°, and a body-centred cubic β-form stable above 880—905°. Measurements of the heat given out in cooling, the resistance, *R*, at 250—940°, and the thermo-e.m.f., *E*, at 50—1020° show that transition occurs very slowly. The true at. heat, C_p, rises from 6·507 at 200° to 8·901 at 817°. From 817° onwards it rises very rapidly, then drops abruptly to 7·525, which is the val. for the β-form and does not vary with temp. Apparently 817—905° is a transition interval. A series of "minor transition points" have also been observed. At these, peculiar hysteresis effects occur on cooling; some, at least, of these points are partly due to the presence of traces of O and N and the production within the metal of oxide films and their partial reduction by the excess of Ti at various temp. These gases also affect the transition $\alpha \rightleftharpoons \beta$-Ti. The modification of the Saladin–Le Chatelier method for the precise measurement of the variation of *E* and *R* with temp. in a high vac. is described. R. C.

Isotherms of methane between 0° and 150° for densities up to 225 Amagat. Calculated specific heat, energy, and entropy in the same region. A. Michels and G. W. Nederbragt (Physica, 1936, 3, 569—577; cf. this vol., 20).—Isotherms of CH_4 have been determined at 25° intervals between 0° and 150° and are represented by an empirical formula. Calc. vals. of the sp. heat, internal and free energies, and entropy are tabulated. O. D. S.

Specific heat of formic acid and its aqueous solutions. A. A. Glagoleva and S. I. Tscherbov (J. Gen. Chem. Russ., 1936, 6, 685—690).—Sp. heat data are recorded for the range 25—80°. R. T.

Amorphous and crystalline forms of rubber hydrocarbon. G. S. Parks (J. Chem. Physics, 1936, 4, 459).—It is suggested that the cryst. rubber hydrocarbon described by Bekkedahl and Matheson (this vol. 417) was in reality a mixture of cryst. material with approx. 70% of amorphous material. The heat of fusion of the pure cryst. material was recalc. as 17·4 g.-cal. per g., which is of the same order of magnitude as the val. for other hydrocarbons of m.p. > 200° abs. H. J. E.

M.p. and b.p. in series of homopolar substances. J. F. Durand (Bull. Soc. chim., 1936, [v], 3, 1382—1388).—When the b.p. (abs. temp.) of A, Kr, and Xe are plotted as abscissæ and those of the corresponding substances PCl_3, $AsBr_3$, and SbI_3 as ordinates, the three points lie on a straight line. The same holds for $SiCl_4$, $GeBr_4$, and SnI_4. Similarly, when the b.p. of He, Ne, A, Kr, and Xe are plotted against those of H_2, F_2, Cl_2, Br, and I, the five points lie on a straight line, but when the m.p. are plotted only the vals. for Cl_2, Br, and I are in alinement. By extrapolation, the halogen at. no. 85 should have b.p. about 684° and m.p. about 572° abs. E. S. H.

Determination of physico-chemical constants. M. Wojciechowski and E. R. Smith (Nature, 1936, 138, 30).—The difference between the b.p. and condensation temp. enables the consts. for the pure substance or azeotropic mixture to be calc. The

b.p. of *iso*-C_5H_{11}·OH and d^{25} for $Pr^{\alpha}OAc$ thus obtained are 131·806° and 0·88299(3) g. per c.c., respectively.
L. S. T.

Vapour pressure of barium. J. A. M. van Liempt (Rec. trav. chim., 1936, 55, 468—470; cf. A., 1935, 1454).—The following expression for the v.p. is obtained: $\log p = -9727/T + 7{\cdot}83$ (p in mm.), and the following data for Ba are calc.: heat of evaporation 44,450 g.-cal. per g.-atom, b.p. 1696°, Trouton's const. 22·6.
O. J. W.

Vapour pressure of deuterium water from 20° to 230°. F. T. Miles and A. W. C. Menzies (J. Amer. Chem. Soc., 1936, **58**, 1067—1069).—V.p. are recorded for D_2O and the differences of latent heat of vaporisation for D_2O and H_2O calc. The v.p. of D_2O and H_2O are identical at about 224°.
E. S. H.

Vapour pressure, b.p., and heat of vaporisation of HDO and H_2O^{18}. E. H. Riesenfeld and T. L. Chang (Z. physikal. Chem., 1936, **B**, **33**, 127—132).—The v.p. of HDO at 100° and of H_2O^{18} at 65—100° have been calc. from the increased concn. of these in the residue after partial distillation of H_2O (cf. A., 1935, 1064). The empirical equations $p_{D_2O}/p_{H_2O} = 1{\cdot}35e^{-259/RT}$ and $p_{H_2O^{18}}/p_{H_2O} = 1{\cdot}013e^{-13/RT}$ have been obtained. The b.p. of HDO and H_2O^{18} are calc. to be $100{\cdot}7_6$° and $100{\cdot}1_3$°, and the mol. heats of vaporisation $\lambda_{H_2O}+130$ and $\lambda_{H_2O}+13$ g.-cal., respectively.
R. C.

Vapour pressure and heat of vaporisation of heavy water. E. H. Riesenfeld and T. L. Chang (Z. physikal. Chem., 1936, **B**, **33**, 120—126).—The excess of the v.p. of H_2O over that of D_2O has been measured at 20—230°. With rising temp. it passes through a max., 82·6 mm., at 170°, and is zero at 225° and negative above. The excess of the heat of vaporisation of D_2O over that of H_2O falls with rising temp., but is always positive.
R. C.

Vapour pressure of ethyl alcohol and toluene as a criterion of purity. F. Schouteden and J. Deveux (Natuurwetensch. Tijds., 1936, **18**, 242—247).—The v.p.-temp. curve of the liquid is determined in a closed space (*e.g.*, in a glass-spring manometer) under such conditions that (1) the vol. of the vapour phase is negligible, (2) the vol. of the liquid phase is negligible compared with that of the vapour. For a pure substance, the two curves are coincident. Curves are recorded for pure EtOH and PhMe. A method of calculating the heat of mixing from v.-p. data is obtained thermodynamically.
D. R. D.

(A) **Isotherms of nitrogen between 200 and 300 atm. and 0° and 150°.** (B) **Calculation of thermodynamic properties of nitrogen up to 3000 atm. between 0° and 150°.** A. Michels, H. Wouters, and J. de Boer (Physica, 1936, **3**, 585—589, 597—604; cf., A., 1934, 355, 837).—(A) Earlier measurements are extended to higher densities (up to 578 Amagat). The results are not accurately represented by either of the empirical formulæ tried.

(B) From the isotherm data the change in internal energy, sp. heat, entropy, and free energy on compression have been calc.
O. D. S.

Determination of coefficient of equilibrium for condensed (gas) systems. S. M. Levinson (Chimstr., 1935, 7, 262—264).—Coeffs. for CH_4, C_2H_4, C_3H_6, C_4H_8, and C_5H_{10} have been derived for the range −90° to 30° and 0 to 50 atm.
Ch. Abs. (*e*)

Thermodynamical researches. N. A. de Kolosovski (Acta Univ. Asiæ Med., 1934, [vi], **1**, No. 7, 3—91).—A thermodynamical treatment of the properties of liquids and vapours.
E. S. H.

Volume energy of real gases (He, Ne, H_2). V. Jacyna (Acta phys. polon., 1934, **3**, 15—32; Chem. Zentr., 1935, ii, 3212).—Data are recorded, and deviations from the ideal gas laws are discussed.
H. J. E.

Röntgenographic measurements of expansion of crystalline masses. W. Büssem [with M. Bluth and G. Grochtmann] (Ber. deut. keram. Ges., 1935, **16**, 381—392; Chem. Zentr., 1935, ii, 2848).—*X*-Ray measurements of lattice parameters are given for MgO, cristobalite, corundum, sillimanite, and SiC from −182° to 1400°.
J. S. A.

Heat conduction by rarefied gases. I. Thermal accommodation coefficient of helium, hydrogen, neon, and nitrogen on glass at 0°. W. H. Keesom and G. Schmidt (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 716; cf. A., 1911, ii, 253; 1933, 1).—The accommodation coeffs. of He (0·336), H_2 (0·283), Ne (0·670), and N_2 (0·855) on glass at 0° have been measured by Schleiermacher's method.
J. L. D.

Heat conductivity of tungsten and cooling effects of leads on filaments at low temperatures. I. Langmuir and J. B. Taylor (Physical Rev., 1936, [ii], **50**, 68—87).—The theory of the effect of the temp. of the leads to a W wire in an evacuated vessel on the temp. distribution and resistance is given, and general equations are given for W filaments up to 600° abs. It is shown that the heat conductivity, λ, may be calc. from determinations of temp. or resistance resulting from the passage of a current through the filament. For low temp. (<600° abs.) it is more convenient to use the resistance. λ at 273° abs. is 1·66 watts per cm. per degree and decreases with rising temp. according to $\log \lambda = 0{\cdot}951 - 80{\cdot}30 \log T$.
A. J. M.

Heat losses from a tungsten wire in helium. W. C. Michels and G. White (Physical Rev., 1935, [ii], 47, 197).—The accommodation coeff. found is 0·092, which becomes 0·069 when corr. for thermal etching produced in cleaning the wire.
L. S. T.

(A) **Conduction of heat by some metals at low temperatures.** H. Bremmer and W. J. de Haas. (B) **Determination of the heat-resistance of mercury at the temperatures obtainable with liquid helium.** W. J. de Haas and H. Bremmer. (C) **Heat conductivity of superconductive alloys.** H. Bremmer and W. J. de Haas (Physica, 1936, **3**, 672—686, 687—691, 692—704).—(A) The heat-resistance (R_h) of Pb has been measured between 2·5° and 77° abs. and of Cu and W between 14° and 22° abs. Below the threshold of superconductivity of Pb R_h has different vals., W_n and W_s, in the presence or absence of a magnetic field of strength sufficient to destroy the superconductivity. $W_n < W_s$. Both pass through min. vals. at about 5° and 8° abs., respectively. The "ideal resistance," R_i, of Pb also passes through a min. R_i of Cu is still decreasing at 14·5° abs. R_i of W appears to tend to a min. at low temp.

(B) Relative vals. of R_h of Hg between 2·5° and 4° abs. are given. W_s and W_n both show a min. val. at about 3·5° abs.

(C) R_h has been measured for alloys of the following compositions: Pb 56, Sn 44 wt.-%, 15—70° abs.: Bi 50, Pb 25, Sn 25 wt.-%, eutectic mixture, 2·6—276° abs.: In–Pb alloys containing 8·6, 50, and 99 wt.-% Pb, 2·5—278° abs. In all cases R_h increases rapidly at low temps. but more slowly than is predicted by theory. O. D. S.

Viscosity of halogen compounds of the elements of group V of the periodic system. (MLLE.) A. I. LICHATSCHEVA and G. P. LUTSCHINSKI (J. Chim. phys., 1936, **33**, 488—491).—The variations with temp. of the viscosities of PCl_3, $AsCl_3$, $SbCl_3$, PBr_3, $AsBr_3$, and $SbBr_3$ follow Batschinski's formula (cf. A., 1935, 438). The limiting vals., ω, of the chlorides are > those of the bromides, and the ω of the group V elements decrease with increase of at. wt. J. G. A. G.

Viscosity of air and the electronic charge. G. KELLSTRÖM (Physical Rev., 1936, [ii], **50**, 190; cf. A., 1935, 1455).—Improved apparatus gave the result $\eta_{20^\circ}=(18201\pm27)\times10^{-8}$ or $\eta_{23^\circ}=(18349\pm27)\times10^{-8}$; this, with Millikan's data, gives $e=(4{\cdot}818\pm0{\cdot}011)\times10^{-10}$ e.s.u. N. M. B.

Measurements of the viscosity of water and water vapour up to the critical region. K. SIGWART (Forsch. Geb. Ingenieurw., 1936, **7**, 125—140).—A flow method for the determination of η of H_2O and H_2O vapour at high pressure and temp. is described. The η of H_2O depends on its *d*, that of the vapour on both its *d* and temp. The slope of the isotherms of η against pressure for H_2O vapour remains practically const. up to the saturation pressure, where an increase occurs. Below 275° the increase in η is small, amounting to only 5% for a pressure increase of 100 atm. The η of H_2O at the crit. point was found to be $3{\cdot}85\times10^{-6}$ kg. sec. per sq. m. R. B. C.

Relationship between the constitution and viscosity characteristics of hydrocarbons. W. R. WIGGINS (J. Inst. Petroleum Tech., 1936, **22**, 305—327).—The viscosity (η) of hydrocarbons in relation to their constitution is considered in the light of published data. It is shown that the fractional η–temp. coeff. $(1/\eta)(\Delta\eta/\Delta t)$ has a linear relationship with log η, *i.e.*, $(\Delta\eta/\Delta t)(1/\eta \log \eta)=$const. This function is approx. const. for the same hydrocarbon, varying from 0·03 to 0·04 for aliphatic hydrocarbons and those of simple cyclic structure, whilst branched and polycyclic hydrocarbons give higher vals. The corresponding expression in kinematic units is regarded as a simple index for classifying viscous hydrocarbons. C. C.

Density of mixtures of some molten electrolytes. V. P. MASCHOVETZ and Z. F. LUNDINA (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 191—212).—The *d* of $MgCl_2$, NaCl, and KCl falls linearly with rise of temp. from 100° to 1000°. The *d*–composition curves of the systems $MgCl_2$–NaCl and –KCl, KCl–$BaCl_2$, and $MgCl_2$–KCl–NaCl have been determined. R. T.

Fused salts. V. A. IZBEKOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 142—152).—A lecture. R. T.

Viscosity of butyric acid–water mixtures. C. R. BURY and J. GRINDLEY (J.C.S., 1936, 1003—1004).—The η–composition curves at −3° to 35° afford no evidence for micelle formation, although anomalous η in the crit. solution region is apparent at −3°. The max. at approx. 70% acid are not accepted as evidence for compound formation. C. R. H.

Dielectric constant of dioxan–water mixtures between 0° and 80°. G. ÅKERLÖF and O. A. SHORT (J. Amer. Chem. Soc., 1936, **58**, 1241—1243).—Data have been obtained for $\lambda=150$ m., using a resonance method. E. S. H.

Solid solutions of methane and krypton. M. VON STACKELBERG, F. QUATRAM, and H. J. ANTWEILER (Z. Elektrochem., 1936, **42**, 552—557).—Thermal analysis and v.-p. determinations show that CH_4 and Kr form an unbroken series of solid solutions. The f.p. and b.p. of all mixtures lie between those of the components. E. S. H.

Aggregative states. II. Connexion between composition and properties in eutectics of binary systems of type I. E. I. ACHUMOV (J. Gen. Chem. Russ., 1936, **6**, 559—575; cf. this vol., 21).—Mathematical. R. T.

Piezometric researches. III. Effect of high pressures on the melting curve of binary mixtures. L. DEFFET (Bull. Soc. chim. Belg., 1936, **45**, 213—250; cf. A., 1935, 688).—Data are recorded for the binary mixtures C_6H_6–$C_{10}H_8$ and C_6H_6–urethane over a wide range of composition. The composition of the C_6H_6–$C_{10}H_8$ eutectic varies only slightly with pressure, and, in general, with increase of pressure, the eutectic is enriched with respect to that component which has the smaller val. of δ (*loc. cit.*). The influence of pressure on the solubility of $Na_2CO_3,10H_2O$ has also been examined. J. G. A. G.

Two eutectic cycles with diphenyl. A. M. VASILIEV (J. Gen. Chem. Russ., 1936, **6**, 555—558).—The eutectics in the systems Ph_2–$COPh_2$, Ph_2–$NHPh_2$, $NHPh_2$–$COPh_2$, and $(CH_2Ph)_2$–Ph_2–$C_{10}H_8$, as determined by Lee and Warner (A., 1933, 228; 1935, 448), agree closely in composition with the requirements of Flavitzki's formula (A., 1906, ii, 152). R. T.

Chemical composition and optical properties of solutions. II. Optical properties of solutions in the quaternary system NH_4Cl–NaCl–KCl–H_2O at 15°. E. I. ACHUMOV and M. P. GOLOVKOV (J. Gen. Chem. Russ., 1936, **6**, 542—548; cf. this vol., 22).—*n*-composition diagrams are recorded. R. T.

System nickel–zinc. W. HEIKE, J. SCHRAMM, and O. VAUPEL (Metallwirts., 1936, **15**, 655—662).—Alloys containing 22—29 and 45—52% Ni have been re-examined by thermal methods. From the results and a detailed consideration of other work, a revised diagram is presented. C. E. H.

Copper–tin alloys. C. Haase and F. Pavlek (Z. Metallk., 1936, **28**, 73—80).—The accepted solid solubility of Sn in Cu is 14% at temp. up to 400°, this val. being obtained with annealed alloys, prolonged ageing of which at ≯400° fails to decompose the solid solution. If, however, such alloys are cold-rolled after annealing and then aged at 300°, pptn. of a Sn-rich phase occurs. From sp. resistance and hardness measurements and from micrographic and *X*-ray analysis of cold-worked alloys after various methods of ageing, it is shown that the true solid solubility of Sn in Cu is 13·5% at 400°, 10·9% at 350°, 5·5% at 300°, 2·8% at 250°, and about 1·2% at 200°. The pptd. phase is Cu_3Sn at $< 370°$ and Cu_3Sn_8 (δ) at $>370°$. Cu_3Sn pptd. at 300° is hexagonal, *a* 2·7523 A., *c/a* 1·5697. The min. amount of cold-work required to produce pptn. is the lower the higher is the degree of supersaturation, and the rate of pptn. is the greater and the period of induction the shorter the higher is the degree of reduction above the min. The rate of pptn. is retarded by crystal recovery and recrystallisation phenomena above 300°. Pptn. is a continuous single-phase process which produces little hardening, but a characteristic change in the microstructure. A. R. P.

Reflecting power of the binary mixed crystal series copper–nickel. P. Bergmann and W. Guertler (Z. tech. Phys., 1935, **16**, 235—236; Chem. Zentr., 1935, ii, 2634).—The selective reflective power of Cu in texturally homogenised Cu–Ni alloys disappears completely with >25% Ni. J. S. A.

***X*-Ray investigation of the transformations in aluminium–silver alloys.** W. Hofmann and K. E. Volk (Metallwirts., 1936, **15**, 699—701).—The work of Ageev and Shoyket (A., 1933, 1110) is confirmed. The β-phase has a body-centred cubic structure, and at 700°, a=3·24 A. C. E. H.

Transformations in eutectoidal copper–aluminium alloys. V. Gridnev and G. Kurdjumov (Tech. Phys. U.S.S.R., 1936, **3**, 135—141).—The transformations in the β-phase of Cu alloys with (*a*) 12%Al and (*b*) 12%Al and 2%Ni have been studied by thermal and dilatometric analysis. The change from the disordered β lattice to the ordered β_1 lattice is accompanied by a small decrease in vol., whereas the martensitic-like transformation $\beta_1 \rightarrow \beta'$ shows a slight increase in vol. On rapid heating of quenched specimens the β′-phase is converted directly into β; to convert β′ into β_1 the quenched alloy must be tempered at 400°, but at 430° the β_1-phase breaks down into eutectoidal $\alpha+\gamma$. When β_1 is reheated at 190° it is reconverted into β′, which then passes back to β_1 at 225° without internal diffusion, and hence the diffusion-less lattice change of the metastable β_1 into β′ is reversible after tempering. A. R. P.

Magnetic investigations of the [precipitation-]hardening of beryllium–nickel alloys. W. Gerlach (Z. Metallk., 1936, **28**, 80—83).—During pptn.-hardening of quenched 2% Be–Ni alloy the *d*, magnetisation, remanence, coercivity, and magnetic transformation point all increase parallel with the hardness; the magnetic hardness produced by pptn. increases with the degree of supersaturation of the original solid solution. These results are explained thus: during pptn. treatment the Be atoms leave the solid solution lattice, which then contracts and being richer in Ni acquires a higher magnetic transformation point. The pptn. temp. is insufficiently high to allow diffusion to fill the lattice gaps by Ni atoms, and hence magnetic hardness is increased. The Ni–Be compound which is pptd. during ageing stabilises the incomplete Ni lattice and renders the increased magnetic hardness relatively insensitive to changes of temp. A. R. P.

***X*-Ray analysis of the homogenous phase in the system Mg–Ni.** F. Bachmetev (Acta Physicochim. U.R.S.S., 1935, **3**, 531).—A correction. The no. of mols. in the unit cell of the compound $MgNi_2$ is 8 and not 16 as previously stated (cf. this vol., 152). O. D. S.

System manganese–carbon and the carburising of manganese alloys. R. Schenck, N. G. Schmahl, and O. Ruetz (Z. Elektrochem., 1936, **42**, 569).—Cementation of Mn in CH_4 at 700—900° has been studied. Mn_3C dissolves 0·5% of C at 800—900°. Higher carbides were not found. In cementing Mn–Fe alloys, Mn_3C stabilises an equiv. amount of Fe_3C; above 900° excess of C is taken into solution. Cementation of Mn is reduced by adding Cu. E. S. H.

Constitution and structure of alloys. A. Portevin (Bull. Soc. chim., 1936, [v], **3**, 1189—1237).—A lecture.

***X*-Ray investigations on the ternary system nickel–copper–zinc.** J. Schramm and O. Vaupel (Metallwirts., 1936, **15**, 723—726).—Previous thermal and micrographic work by Schramm (Diss., Freiberg, 1934) is extended to the examination of the phases which occur at room temp. C. E. H.

Alloys of iron, manganese, and carbon. XV. Ternary diagram and general summary. F. M. Walters, jun., and C. Wells (Trans. Amer. Soc. Met., 1936, **24**, 359—374).—Previous work is summarised. W. P. R.

***X*-Ray investigation of the iron–chromium–silicon phase diagram.** A. G. H. Andersen and E. R. Jette (Trans. Amer. Soc. Met., 1936, **24**, 375—419).—The Fe-rich portion of the ternary diagram Fe–Cr–Si has been studied by *X*-ray methods. The parametric surface of Fe-rich solid solutions has been developed with considerable accuracy, and the range for which the α-Fe phase is homogeneous at 600°, 800°, and 1000° has been determined. The boundary consists of three sections characterised by (*a*) the $(Fe,Cr)_3Si_2$ phase, (*b*) the Cr_3Si phase, and (*c*) the solid solution phase which dissolves up to 10% Si. This phase is formed by pptn. from the binary and ternary α-solid solutions. W. P. R.

Transformation in 18 : 8 [chromium–nickel] austenitic steel. I. Magnetic investigation of the $\gamma \rightleftharpoons \alpha$ transformation. G. Akimov and L. Pevsner. **II. Investigation of the transformation by thermoelectric method.** G. Akimov and

N. Tomashov. **III. Thermal expansion of cold-worked 18 : 8 steels. IV. The $\gamma \rightarrow \alpha$ transformation in 18 : 8 austenitic steel deformed by twisting at different temperatures.** G. Akimov and J. Friedmann. **V. Thermal analysis of deformed and hardened stainless steel.** G. Akimov and N. Tomashov (Tech. Phys. U.S.S.R., 1936, **3**, 142—148, 149—154, 155—157, 158—164, 165—175).—I. When austenitic 18 : 8 stainless steel is cold-rolled, transformation of γ into α starts along the grain boundaries and slip planes and reaches 45% after a reduction of 80% in thickness. On subsequent heating of the cold-worked metal the amount of α begins to increase at 250° and the rate of transformation increases with the degree of reduction, a definite relation between α and γ being established for a definite temp. and a definite degree of reduction. At 445° reconversion of α into γ begins irrespective of the degree of reduction, but above 475° there is a definite equilibrium between the α and γ for each temp., and this varies with degree of reduction up to about 600°, above which it again becomes independent of degree of reduction, since at this temp. α has practically disappeared.

II. Measurements of the e.m.f. between deformed and undeformed 18 : 8 steel show a sudden change at 485—700° due to the $\alpha \rightarrow \gamma$ transformation. Increase in degree of reduction from 48 to 71% lowers the temp. at which carbide pptn. occurs from 730° to 705°. The thermoelectric power–temp. curve for deformed steel resembles closely the magnetic saturation–temp. curve above 450°.

III. Dilatometric curves for cold-worked 18 : 8 steel show that a contraction occurs at 500° due to the $\alpha \rightarrow \gamma$ change which is not affected by degree of reduction and an inflexion at 650° probably due to carbide pptn.

IV. The degree of work-hardening of 18 : 8 steel produced by twisting varies only slightly between 20° and 470°; as the deformation temp. is raised to 150° the magnetic saturation decreases sharply and at higher temp. approaches zero asymptotically, indicating that transformation of γ into magnetic α practically ceases at 150°. Twisting at room temp. produces a more fine-grained structure, but tends to rupture the grains, whereas twisting at 450—470° produces no deformation of the microstructure and no refinement of the grain structure.

V. Thermal analysis of cold-worked 18 : 8 steel shows a heat effect due to removal of elastic stress starting at 490° and reaching a max. at 540°, a second effect due to carbide pptn. starting at 650° and reaching a max. at 695°, and a third effect due to the beginning of recrystallisation at 800°. On reheating the steel after quenching from 1200° heat effects occur at 435° and 540° due to stress removal and at 700° due to carbide pptn. A. R. P.

Low-temperature diffusion of solid aluminium into iron. L. G. Hall (Physical Rev., 1935, [ii], 47, 418—419).—A review of data relating to the diffusion of Al into Fe. L. S. T.

Diffusion in solid metals and its relation to other properties. W. Seith and E. A. Peretti (Z. Elektrochem., 1936, **42**, 570—579).—The diffusion velocities of Cu, Cd, In, Sn, and Sb in Ag at 650—895° have been determined by spectrum analysis. The results confirm those reported for diffusion in Pb (A., 1935, 158). E. S. H.

Diffusion of gases through metals. III. Degassing of nickel and diffusion of carbon monoxide through nickel. C. J. Smithells amd C. E. Ransley (Proc. Roy. Soc., 1936, **A**, **155**, 195—212).—The gas evolved by heating commercial Ni in a vac. or in H_2 is mainly CO. The measured rate of diffusion of CO through Ni is too small to account for the rate at which gas is evolved in the degassing process; it is therefore suggested that the CO is generated from C and O_2 contained in the Ni. Measurements have also been made of the diffusion of C and O_2 through Ni. The rate of diffusion of O_2 is much < that of C, but it would seem that the rate of diffusion of C is the controlling factor in the rate at which CO is evolved. L. L. B.

Diffusion of sucrose in highly concentrated solutions. A. Mertens (Bull. Ass. anc. Étud. Louvain, 1935, **35**, 107—110; Chem. Zentr., 1935, ii, 3311).—The diffusion coeff. is tabulated from 18·5° to 160°. H. N. R.

Vaporisation of boric acid in the cold with the vapours of the lower homologues of primary alcohols. M. Arquet (Bull. Soc. chim., 1936, [v], **3**, 1422—1424).—H_3BO_3 vaporises rapidly from solutions in MeOH at room temp.; in EtOH solutions the loss of H_3BO_3 is less. When coal gas, containing the vapour of MeOH, EtOH, or $Pr^{\alpha}OH$, is passed over cryst. H_3BO_3, the latter is volatilised, the gas burning subsequently with a green flame. E. S. H.

Volatility and dehydration of boric acid. M. von Stackelberg and F. Quatram (Z. Elektrochem., 1936, **42**, 551).—The influence of temp. (110—170°) and H_2O-v.p. (100—760 mm.) on the volatilisation of H_3BO_3 in H_2O vapour has been determined. H_3BO_3 vaporises as such and has a definite "solubility" in H_2O vapour, which is independent of the pressure. The main influence of H_2O is to prevent dehydration to HBO_2, which is non-volatile. E. S. H.

Solubility of slightly soluble electrolytes. M. Haïssinski (Acta Physicochim. U.R.S.S., 1935, **3**, 517—528).—Methods used in the measurement of the solubilities of the hydroxides and sulphates of the heavy metals are criticised. The results of different methods are so discordant that the measured vals. cannot be regarded as characteristic consts. O. D. S.

Solubility of alkaline-earth fluorides in acids. I. Tananaev and S. Tschrelaschvili (J. Gen. Chem. Russ., 1936, **6**, 606—611).—The solubility of CaF_2, SrF_2, and MgF_2 is given by $S=(L[H^{\cdot}]^2/4K^2+1)^{1/3}-M/1000$, where S is g. of fluoride of mol. wt. M in 1 ml. of solution, L is the solubility product, and K the dissociation coeff. of HF. The formula does not apply to BaF_2. Formulæ for deriving the vals. of L and K at different p_H are given. R. T.

Solubility of precipitates in acids. A. K. Babko (Bull. Sci. Univ. Kiev, 1935, **1**, 155—161).—Expressions are derived, whereby the solubility of sparingly sol. salts (BaC_2O_4, CaC_2O_4) in presence of excess of cation or precipitant may be calc. Experimental results agree with theory in presence of excess of $H_2C_2O_4$, but not of $Ba^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$. R. T.

[Solubility of] nitrates of group II metals in liquid ammonia. M. A. PORTNOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 93—104).—The solubility of $Ca(NO_3)_2,4H_2O$ in liquid NH_3 increases between −70° and 70° and shows a break at −46°, corresponding with the transition to $Ca(NO_3)_2,4NH_3$; at 25° the solid phase is $Ca(NO_3)_2,6\cdot5NH_3$. Solubility data are also recorded for $Sr(NO_3)_2$ and $Ba(NO_3)_2$; the solubilities are in the order Ca>Sr>Ba at −50°, and in the inverse order at 50°. Sr and Ba nitrates do not combine with NH_3 at 0°; they combine with 2·5 and $4NH_3$, respectively, at −12°, and with $8NH_3$ at −25°. Curves connecting solubility with conductivity are recorded. R. T.

Solubility of organic compounds in water. A. E. VAN ARKEL and S. E. VLES (Rec. trav. chim., 1936, **55**, 407—411).—Data are recorded for 9 chloroethanes and for *s*-$C_2H_4Br_2$ in H_2O at 0—50°. The results are discussed in reference to the dipole moments of the solutes and the formula (cf. A., 1934, 1064) expressing the relation between the heat of mixing and the cohesion energies of the two components. O. J. W.

Salting out. Influence of ammonium salts on solubility of nicotine. B. V. J. CUVELIER (Z. anal. Chem., 1936, **105**, 325—328).—$(NH_4)_2SO_4$ has the largest salting out effect. J. S. A.

Equilibria in salt systems with deuterium water. F. T. MILES, R. W. SHEARMAN, and A. W. C. MENZIES (Nature, 1936, **138**, 121).—When referred to the same no. of mols. of solvent the solubility of KCl in D_2O is < that in H_2O by approx. 7% at 30°, 3·6% at 100°, and 1·5% at 180°. At 10°, $CuSO_4,5D_2O$ is approx. 12% less sol. in D_2O than is $CuSO_4,5H_2O$ in H_2O, and approx. 1·2% at 96°, where both salts are transformed into the triaquo-forms. The relations between the solubility curves for $SrCl_2,6H_2O$, $SrCl_2,6D_2O$, $SrCl_2,2H_2O$, and $SrCl_2,2D_2O$ are also described. L. S. T.

Connexion between separate and reciprocal solubility of components in systems involving double decomposition. E. I. ACHUMOV (J. Gen. Chem. Russ., 1936, **6**, 691—696).—Theoretical. R. T.

Dissolution of elements in molten $AlCl_3$–NaCl. V. A. PLOTNIKOV and N. S. FORTUNATOV (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 123—128).—The solubility of Hg, P, Mn, W, Mo, Cu, Si, and S in molten 1 : 1 $AlCl_3$–NaCl has been measured at 150—370°. Except in the case of S, chemical reaction does not take place between the solutes and the solvent. R. T.

Formation and growth of a new phase in relation to the influence of vectoral properties of a substance, and of external factors. IV. Influence of solvent and of admixtures on the form of the crystals separating. V. Influence of an electric field on the linear velocity of crystallisation in supercooled liquids. S. S. URAZOVSKI and J. S. ROZUM (Ukrain. Chem. J., 1936, **11**, 127—135, 136—142).—IV. The size and shape of crystals separating from supersaturated solutions of NaCl in H_2O or EtOH, CdI_2 in H_2O, MeOH, EtOH, PrOH, BuOH, Et_2O, $COMe_2$, $CHCl_3$, or PhMe, and of $CO(NH_2)_2$ in H_2O, EtOH, PrOH, BuOH, Et_2O, MeCHO, CCl_4, C_6H_6, PhEt, or $PhNO_2$ vary according to the nature of the solvent, and of other substances (PhOH and $Bu^{\beta}CO_2H$) present. The phenomena are interpreted on the basis of selective adsorption on different crystal edges.

V. The rate of crystallisation of salol, but not of $COPh_2$, is reduced in an electric field; the effect is ascribed to differences in the relative proportions of the different polymorphs of salol present. R. T.

Partition coefficient of iodine between water and carbon tetrachloride. G. HERRERO (Anal. Fís. Quím., 1936, **34**, 549—552).—The partition coeff. increases from 75·07 to 84·7 as the [I] in the CCl_4 layer increases from 1·27 to 15·45 g. per litre. L. A. O'N.

Distribution of nicotine between water and organic solvents. N. A. DE KOLOSOVSKI and F. S. KULIKOV (Acta Univ. Asiæ Med., 1935, [vi], **1**, No. 8, 1—28).—Distribution coeffs. for nicotine between H_2O and C_6H_6, xylene, decalin, light petroleum, CCl_4, $CHCl_3$, $CHBr_3$, $C_2H_4Br_2$, PhBr, $PhNO_2$, Et_2O, *iso*amyl ether, *iso*-$C_5H_{11}\cdot OH$, $CH_2Ph\cdot OH$, *m*-cresol, *cyclo*hexanone, and CS_2, respectively, and between glycerol and CS_2 at 25°, have been determined. The results are discussed. E. S. H.

Adsorption of argon and nitrogen from the lowest to the highest pressures by active carbon. A. VON ANTROPOFF [with F. STEINBERG, F. KALTHOF, L. SCHMITZ, and R. SCHAEBEN] (Z. Elektrochem, 1936, **42**, 544—547).—Adsorption has been determined from −160° to 200° and from 0·005 to 200 atm. Adsorption increases linearly with increasing pressure at low pressures; at higher pressures and low temp. a max. is reached, whereas at still higher pressures adsorption decreases and eventually almost reaches zero. The apparent contradiction to Langmuir's equation is discussed. E. S. H.

Adsorption of radium emanation at low temperatures. L. WERTENSTEIN (Acta phys. polon., 1934, **3**, 469—484; Chem. Zentr., 1935, ii, 3058—3059).—The life period of the absorbed material and the dependence of the adsorption equilibrium on the temp. have been determined. H. J. E.

Influence of platinum on the adsorption characteristics of charcoal in solutions of electrolytes. S. LEVINA, A. FRUMKIN, and A. LUNEV (Acta. Physicochim. U.R.S.S., 1935, **3**, 397—412).—The effects which result from platinising can be reproduced by the mechanical mixing of Pt with the charcoal. It is suggested that the action of the Pt is purely electrochemical; the potential of the Pt, acting as a H_2 electrode, is communicated to the charcoal and determines its adsorption capacity. O. D. S.

Measurements of adsorption at the air–water interface by the microtome method. J. W. MCBAIN and R. C. SWAIN (Proc. Roy. Soc., 1936, A, 154, 608—623).—The microtome method (A., 1932, 331) is shown to give reproducible quant. measurements of the abs. amount of adsorption in the air–H_2O interface for all types of solutions. The results for positive adsorption of PhOH and of $CH_2Ph\cdot CH_2\cdot CO_2H$, and for negative adsorption of NaCl agree closely with the predictions of the Gibbs theorem. L. L. B.

Adsorbent properties of barium sulphate. I. M. Kolthoff (Bull. Soc. chim. Belg., 1936, 45, 270—278).—The data and conclusions of de Brouckère (cf. this vol., 423) are disputed. J. G. A. G.

Adsorbent properties of barium sulphate. (Mlle.) L. de Brouckère (Bull. Soc. chim. Belg., 1936, 45, 279—285).—A reply to Kolthoff (cf. preceding abstract). J. G. A. G.

Adsorption of organic substances at crystal surfaces. IV. Adsorption of sodium oleate and nonoate by cinnabar. N. A. Held and I. A. Chainski (Kolloid-Z., 1936, 76, 26—33; cf. A., 1935, 1069).—Potentiometric titrations show that a bimol. layer of the soap is adsorbed at the surface of cinnabar. E. S. H.

Adsorption of dyes on glass. J. Lenoir (Document. sci., 1935, 4, 193—199; Chem. Zentr., 1935, ii, 2933).—With very dil. solutions, the amount of dye adsorbed rises steeply with increasing concn., reaching a const. max. val. at fairly low dye concn. With Me-violet a bimol. adsorbed layer is formed. J. S. A.

Sorption of vapours by gels of hydrates of the oxides of aluminium, iron, and titanium. I, II. E. V. Alexeevski and G. M. Belotzerkovski (J. Gen. Chem. Russ., 1936, 6, 370—381, 382—389).—I. Max. sorptive capacity for $CCl_3\cdot NO_2$ and C_6H_6 vapours is obtained by drying $Fe(OH)_3$ gel at 100—200°, $Al(OH)_3$ gel at 120—240°, and TiO_2 gel at 200°.

II. The sorptive power of $Al(OH)_3$ gel for C_6H_6 vapour is $>$ that of $Fe(OH)_3$ gel, and for H_2O vapour is $>$ that of $CaCl_2$, P_2O_5, and SiO_2 gel. Adsorption of H_2O proceeds according to the Langmuir equation. R. T.

Periodic phenomena in diffusion and adsorption. II. Experiments without membranes. H. Waelsch and S. Kittel (Kolloid-Z., 1936, 76, 19—26; cf. this vol., 284).—The concn. of aq. NaCl or $CaCl_2$ undergoes periodic changes with time after addition of $BaSO_4$. This behaviour is traced to periodic adsorption of the electrolyte by the ppt. The periodic effect is destroyed by addition of $NaNO_3$, NaOH, or H_2S, but not by HCl or H_2SO_4; it depends also on the method of prep. of $BaSO_4$, and on the relation of the amount of adsorbent to the electrolyte concn. E. S. H.

Constitution of the surface of active carbon. E. O. K. Verstraete (Natuurwetensch. Tijds., 1936, 18, 107—113).—Diamond sols are negatively charged and do not become positive even after long activation in CO_2 at 1050°. The results are in accordance with Kruyt's theory of electron shift for positive C. S. C.

Surface oxide films. E. J. W. Verwey and J. H. de Boer (Rec. trav. chim., 1936, 55, 675—687).—Theoretical. In the oxides formed by adsorption of O on alkaline-earth metals the surface oxide mols. are at. rather than ionic, yet the linking is sufficiently polar to produce a double layer, with the negative coating outside. There is an activation energy, E, because the O_2 mol. must be dissociated and the reacting atoms brought into an excited state. For C this is $>$ for metals owing to the O atoms each being bound by two C atoms and C–C distance in the graphite lattice being small. The positive charge of outgassed C in contact with air and H_2O is attributable to its adsorbing O and behaving as an O electrode. A negative ζ-potential combined with a positive Nernst (air) potential on C and on noble metals can be explained by the presence of a surface oxide layer with a large positive potential drop (cf. A., 1935, 1069). R. C.

Thermomechanics of the surface film. I. General; pure substances. II. Adsorption formula. III. Mixed phases. J. E. Verschaffelt (Bull. Acad. roy. Belg., 1936, [v], 22, 373—389, 390—401, 402—411).—Theoretical. A. J. M.

Surface development of active zinc oxide. G. Graue and R. Köppen (Z. anorg. Chem., 1936, 228, 49—56).—Changes in the surface of ZnO with various thermal treatments have been followed by the Hahn emanation method (A., 1935, 32). The emanation evolved increases rapidly after heating to 300°, decreases with pretreatment at 350—1000°, and rises somewhat after the specimen has been heated to $>$1000°. This agrees with the observed optimum catalytic activity of ZnO after heating to 300°. The adsorption of indigotin from C_6H_6 solution is also a max. for ZnO previously heated at 300°. X-Ray photographs are given for specimens of ZnO after various heat-treatments. The adsorption of emanation by ZnO is diminished by long heating. It is a max. after heating at 300°. H. J. E.

Stability of a surface of contact between two phases. Concept of epiphases in mutual equilibrium. New enunciation of the phase rule. L. Gay (J. Chim. phys., 1936, 33, 476—487).—Theoretical. When a surface of contact between two phases becomes unstable, two or more epiphases in mutual equilibrium appear, and the variance, V, of the system of n components, ϕ phases, ϕ' epiphases, and s surfaces of contact is $V=n-\phi-\phi'+s+2$. The theory is of general application to singular points in interfacial tension curves (cf. A., 1926, 348; 1932, 1200; 1935, 1071). J. G. A. G.

Relations between the adhesion of particles of microscopic size and the activity coefficients of the electrolytes. A. von Buzágh (Kolloid-Z., 1936, 76, 2—9).—The adhesion of quartz particles of $14\cdot2\,\mu$ diameter to a wall of polished quartz has been determined in solutions of different electrolytes by the tilting-plate method. With neutral salts containing uni- and bi-valent cations the adhesion decreases with increasing activity coeff.; solutions of ter-, quadri-, and sexa-valent cations reverse the charge on the quartz particles, and the curve connecting adhesion with activity coeff. shows a max. and a min. With salts of multivalent cations the relations are complicated by the effects of hydrolysis.

E. S. H.

Permeability of membranes. I. Theory of ionic permeability. II. Experiments with artificial selective membranes. K. H. Meyer and J. F. Sievers (Helv. Chim. Acta, 1936, **19**, 649—664, 665—677).—I. A quant. theory of the ionic selectivity of membranes is given, in which the membrane is regarded as a network of chains carrying laterally fixed ionised groups. The permeability depends on (*a*) the concn. of the fixed ions, (*b*) the mesh of the network, (*c*) the external concn. of the electrolyte, and (*d*) the solubility of the ions in the membrane.

II. Methods are described for preparing neutral, acidic, basic, and amphoteric membranes, which have been studied. The results are interpreted in the light of the authors' theory. The selectivity of biological membranes and their powers of absorbing certain dyes have been correlated. T. G. P.

Cryoscopic constants. J. F. Durand and L. Waï-Hsun (Bull. Soc. chim., 1936, [v], **3**, 1389—1391). —The relation $K'=0{\cdot}0015MT'$, where K' is the cryoscopic const., M the mol. wt., and T' the abs. m.p., is deduced theoretically and confirmed experimentally for several org. substances. Exceptions are traced to association or other anomalies.

E. S. H.

Nature of some dilute and concentrated non-electrolytes. B. H. van Ruyven (Rec. trav. chim., 1936, **55**, 471—491).—F.p., b.p., and osmotic pressure data for aq. solutions of MeOH, sucrose, glucose, mannitol, α-methylglucoside, and dulcitol are discussed. In many cases the depression of the f.p. (Δ_f) and the elevation of the b.p. (Δ_b) are given, even for conc. solutions, by $\Delta_f=1{\cdot}85N_w$ and $\Delta_b=0{\cdot}52N_w$, where N_w=g.-mols. solute per 1000 g. H_2O. The osmotic pressure is given by $P=22{\cdot}41N_w\times T/273$. Deviations from these equations are due mainly either to formation of complexes of solute mols. or to hydration of the solute mols. O. J. W.

Non-aqueous solutions. I. A. Kablukov (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 13—28).—A lecture. R. T.

Non-aqueous solutions. I. Ternary systems. V. A. Plotnikov (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 29—45).—A review.

R. T.

Specific heat of non-electrolytes in solution, and the effect of the dielectric constant of the solvent on the vibrational state of their molecules. K. Bennewitz and L. Kratz (Physikal Z., 1936, **37**, 496—511).—Results obtained by Heydweiller's method for CsCl and LiCl agree with those obtained by other methods. The sp. heats of aq. solutions of $CO(NH_2)_2$, glycerol, quinol, dioxan, glucose, lactose, sucrose, and solutions of some of these substances in other solvents of known dielectric const. have been determined. The solute usually has a larger mol. heat in solution than in the pure state. In explanation it is assumed that the dielectric const. of the solvent affects the directional forces of the oscillators in the solute mols. Calculation of the mol. heat from the lowering of frequency due to the dielectric effect and the existence of dispersion gives satisfactory results for glucose and sucrose. This lowering of frequency could be demonstrated by an examination of the Raman lines of the solutions, which should show a displacement. A. J. M.

Dielectric constants of extremely dilute solutions. F. E. Hoecker (J. Chem. Physics, 1936, **4**, 431—434; cf. A., 1935, 1318).—Measurements by the heterodyne beat method are recorded for C_6H_6 and CCl_4 solutions of EtOH at mol. fraction vals. from 0·01 to 0·00007. Effects of association are absent in this concn. range. Derived vals. of the mol. polarisation of EtOH at 24·5° agree with measurements made on EtOH vapour. The electric moments of EtOH in C_6H_6 and CCl_4 solution are $1{\cdot}700\pm0{\cdot}006\times10^{-18}$ and $1{\cdot}674\pm0{\cdot}005\times10^{-18}$, respectively. Vals. of d for dil. solutions of EtOH in C_6H_6, CCl_4, and CS_2 are recorded. H. J. E.

Dipole moments of molecules in solution. S. H. Bauer (J. Chem. Physics, 1936, **4**, 458—459).—Fluctuation for polar mols. dissolved in a non-polar solvent is discussed. H. J. E.

(A) Optical rotation of alkaline solutions of sucrose. (B) p_H of solutions of calcium hydroxide in water and aqueous sucrose. K. Smoleński (Rocz. Chem., 1936, **16**, 270—280, 281—287).—(A) [with W. Kozłowski]. The fall in $[\alpha]_M$ with increasing p_H is due to formation of uni- and bi-valent anions of sucrose, of $[\alpha]_M$ 20·6° and 18·4°; the vals. found agree with the view that sucrose is a dibasic acid, with $k_1=3\times10^{-13}$ and $k_2=3\times10^{-14}$.

(B) [with S. Porejko]. The p_H vals. found are in conformity with the above view. R. T.

Behaviour of methyl-red in alcohol–water solution. F. Reimers (Z. anorg. Chem., 1936, **228**, 33—43).—The absorption curves of Me-red in acid, alkali, and buffered EtOH–H_2O solutions (20—85% EtOH) have been measured spectrophotometrically. Absorption coeffs. for the isoelectric form (I) and indicator exponents for Me-red in 20—85% EtOH solution are calc. The change of indicator exponent with [EtOH] suggests that (I) is an uncharged mol.

H. J. E.

Refraction of solutions of electrolytes, and ionic association. A. I. Brodski, N. S. Filippova, and G. M. Scherschever (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 72—79).—Refraction data for 0—0·12*N*-KCl and -NaCl support the theory of complete ionisation. R. T.

Nature of electrolytes in non-aqueous solutions. M. I. Usanovitsch (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 46—49).—Conductivity is associated with compound formation.

R. T.

Solvation in non-aqueous solutions. V. S. Finkelschtein (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 50—53; cf. preceding abstract).—Usanovitsch's results are compatible with solvation rather than with compound formation.

R. T.

Optical behaviour of dissolved ions and its significance for the structure of solutions of

electrolytes. III. Optical absorption of sodium eosinate. G. Kortüm (Z. physikal. Chem., 1936, **B**, **33**, 1—22; cf. this vol., 425).—The extinction coeffs., ε, for the various absorption bands rise rapidly with the concn., *c*, except when this is very small, when they remain const. This effect is apparently connected with the decrease in fluorescence with rise in *c*. The effect of foreign salts on ε indicates that the above variation of ε is due, not to deformation of the eosin anions (I) in the Coulomb field of the ionic atm. nor to ionic association of (I) with cations, but to association of (I) with each other under the influence of van der Waals forces. This association is detectable at concns. as low as $3\times10^{-6}M$. R. C.

Dielectric constants of amphoteric electrolytes. G. Halbedel (Z. physikal. Chem., 1936, **B**, **33**, 83—108).—Dielectric consts., ϵ, have been measured at 20—50° by a resonance method with a frequency of $\sim10^8$ hertz. For aq. solutions of antipyrine, *p*-$NH_2\cdot C_6H_4\cdot CO_2H$, theobromine, caffeine, 7-methylpurine, and pyocyanine ϵ is $\ngtr$ for pure H_2O; the possibility of a zwitterion structure for the first two substances thus seems improbable. For solutions of NH_2-acids and betaines in H_2O and EtOH ϵ is $>$ that of the solvent by an amount $\Delta\epsilon$ which increases linearly with the concn. up to a crit. concn., *c*, at which mutual interaction of the mols. becomes effective; *c* depends on the length and dipole moment of the zwitterion. $\Delta\epsilon$ per mol. of solute is approx. $\propto$ the no. of members in the chain between the positive and negative charge. The technique of measuring ϵ is discussed. R. C.

Complex aquo-phosphate ions with several [solvent molecule] shells. H. Brintzinger and C. Ratanarat (Z. anorg. Chem., 1936, **228**, 61—64; cf. A., 1935, 824).—Determinations of the ionic wt. of PO_4''' by the dialysis method are recorded for p_H 2·0—14·2, using S_2O_3'' as the reference ion. Vals. corresponding with $[H_2PO_4(H_2O)_4]'$ at p_H 2 and $[PO_4(H_2O)_{18}]'''$ at p_H 14·2 have been obtained. The constitution of these ions is discussed. H. J. E.

Methods of dialysis. IV. Independence of ionic weight determination on the p_H of the solution to be dialysed. H. Brintzinger, C. Ratanarat, and W. Eckardt (Z. anorg. Chem., 1936, **228**, 77—82; cf. A., 1935, 579).—It is shown by measurements on various ions (*e.g.*, $[Fe(CN)_6]'''$, $[Co(NH_3)_4SO_4]^{\cdot}$) that the ionic wt. is independent of the reference ion used and is the same whether the medium is alkaline, neutral, or acid. H. J. E.

Formation of aërosols. I. Technique. Sulphuric acid clouds. N. Fuchs and N. Oschman (Acta Physicochim. U.R.S.S., 1935, **3**, 61—78).—A method for preparing aërosols with reproducible particle concn. and particle size consists in rapidly mixing two air streams containing substances which will react to give the desired aërosol, followed by rapid expansion. In this way coagulation is almost entirely avoided. The production of H_2SO_4 clouds by mixing air streams containing SO_3 and H_2O is described. The radius of the particles was $1\cdot2$—$1\cdot5\times10^{-6}$ cm. A. J. M.

Preparation of colloidal gold, and its detection in very small quantities. D. C. Dalmas and E. C. Stathis (Praktika, 1935, **10**, 106—110; Chem. Zentr., 1935, ii, 2644).—AuCl is reduced by alcoholic phenolphthalein at 35—40° to a violet Au sol. The reaction may be used for the detection of Au. J. S. A.

Synthesis of hydrosols of sparingly soluble metal salts by electrolysis. III. Copper arsenate and arsenite hydrosols. B. G. Saprometov and S. P. Kamsolovo (Kolloid-Z., 1936, **76**, 46—54; cf. A., 1934, 1305).—The prep. of negatively-charged $Cu_3(AsO_4)_2$ and $Cu_3(AsO_3)_2$ sols by electrolysis of Na_3AsO_4 or Na_3AsO_3 with a Cu anode and Pt cathode under fixed conditions of c.d., concn., and temp. is described. Positively-charged sols of $Cu_3(AsO_4)_2$ have been prepared from $Zn_3(AsO_4)_2$ and very dil. solutions of Cu salts. The ζ-potential and the resistance to coagulation by KCl have been determined. Tests on the use of these sols as insecticides have been carried out. E. S. H.

TiO_2 hydrosols. R. Wintgen and K. Lins (Angew. Chem., 1936, **49**, 489—492).—Dialysis of 1—3% $TiCl_4$ solution yields sols more conc. than those prepared by Graham's method and of finer particle size than the method of grinding and suspending. Relatively clear sols are also obtained by pptg. TiO_2 from aq. $TiCl_4$ with NH_3 and peptising the ppt. with NaOH. The sp. conductivities of the sols prepared in different ways have been measured and the average no. of TiO_2, Cl', and H_2O mols. per micelle are calc. J. W. S.

Nature of cellulose ester solutions. S. Glückmann (Kolloid-Z., 1936, **76**, 84—95).—Benzylcellulose has been fractionated by adding excess of EtOH to solutions in C_6H_6–EtOH. The viscosity and solubility of the fractions have been determined, and little difference in composition and properties is observed. The crit. amounts of excess of C_6H_6 or EtOH required to coagulate the solutions at different temp. and the influence of variation in the proportions of C_6H_6 and EtOH on the viscosity and vol. of the solution have been determined. The results are discussed in relation to adsorption and solvation phenomena. E. S. H.

Viscosity of suspensions and solutions. VII. Viscosity of sphere suspensions. R. Simha (Kolloid-Z., 1936, **76**, 16—19; cf. this vol., 679).—Mathematical. E. S. H.

Pressure viscosimetry of kaolin suspensions. G. Fuchs (Acta Physicochim. U.R.S.S., 1935, **3**, 137—146).—A new form of capillary viscosimeter is described. The relation between the viscosity, η, of suspensions of kaolin and structure formation has been examined. η at first increases with time and then decreases. This is attributed to aggregation, which may be supposed to occur in two stages. The primary aggregates cease to be formed after a time, and then a looser secondary aggregation occurs, accounting for the decrease in η. The greater is the initial degree of dispersion the more intensive is the structure formation. Dilution causes the destruction of the suspension. Addition of dehydrating agents

(EtOH) encourages structure formation and produces an increase in η. A. J. M.

Refraction of light by colloidal solutions. I. Arsenic and antimony trisulphide sols. A. S. Menon (Kolloid-Z., 1936, **76**, 9—15).—Light refracted by freshly-prepared As_2S_3 sols is almost completely plane-polarised. The degree of polarisation for long $\lambda\lambda$ is $>$ for short $\lambda\lambda$. Rayleigh's law has been confirmed for sols of particle size between 23 and 108 mμ. After keeping the sol for about 14 days, the refracted light contains about 10% of unpolarised light. Sb_2S_3 sols show a weak, unpolarised component in the refracted light. E. S. H.

Viscosimetric investigations of structure formation in ferric hydroxide sols. III. Destruction of ferric hydroxide sols on dilution. G. Fuchs and Z. Kamsolova (Acta Physicochim. U.R.S.S., 1935, **3**, 127—136).—The destruction of young and aged conc. $Fe(OH)_3$ sols and gels on dilution has been studied. The effect of adding $FeCl_3$ was also examined. The viscosity data indicate the existence of structures of different ages and solidity in the sol particles, which may be termed primary and secondary structures. The mechanism of destruction consists in the breakdown of secondary structures and displacement of the adsorption equilibrium with dilution. A. J. M.

Effect of dilution of ferric hydroxide sols. K. Jabłczyński and B. Sawoniak (Rocz. Chem., 1936, **16**, 301—305).—The velocity of coagulation of $Fe(OH)_3$ sols is given by $k\times10^{-3}=63{\cdot}3c^{1{\cdot}5}$, where c is the concn. of $Fe(OH)_3$. The charge and dimensions of the particles are not affected by dilution. R. T.

Electrochemistry of platinum sols. I. Preparation of the sols. N. Bach and N. Balaschova (Acta Physicochim. U.R.S.S., 1935, **3**, 79—96).—Pt sols have been prepared by the arc method with O_2, H_2, and air, respectively, above the H_2O in which dispersion takes place. The O_2–Pt sol is brown, and the conductivity of the sol is $\not>$ that of the H_2O in which it is dispersed. The H_2–Pt sol is moderately stable and is grey. The conductivity of a H_2–Pt sol decreases when saturated with O_2; that of an O_2–Pt sol increases when saturated with H_2. The conductivity of an air-Pt sol is about 15 times that of the H_2O in which it is dispersed, indicating the formation of foreign electrolytes, and not only $H_2Pt(OH)_6$. When H_2SO_4 was added to the H_2–Pt sol, which was then saturated with O_2, conductivity measurements show that the adsorption is essentially similar to that at platinised Pt electrodes, each particle of sol acting as a small gas electrode. Cataphoresis experiments show that the particles of the H_2–Pt sol are negatively charged, the cataphoretic velocity being 3—4 μ per sec. per volt per cm. A. J. M.

Electrochemical properties of highly purified silica sols. A. I. Baibaiev and V. A. Kargin (Acta Physicochim. U.R.S.S., 1935, **3**, 97—118).—SiO_2 sols obtained by hydrolysis of $SiCl_4$ cannot be prepared in the pure state by electrodialysis through a carefully purified parchment-paper membrane. The acidic properties of "pure" SiO_2 sols are due to acid (usually HCl) in the intermicellar liquid of the sol. SiO_2 sols obtained by oxidation of SiH_4 by O_3 in aq. solution possess no acidic properties, and only a very small quantity of compensating ions in the outer shell of the double layer. The stability of such pure SiO_2 sols is maintained solely by the lyophilic properties of H_2SiO_3, but HCl exerts a stabilising action. The cataphoretic velocity and the ζ-potential are small, and are dependent to a high degree on the purity of the sol. A. J. M.

Effect of supersonic waves on the viscosity of colloids. O. Kimura (J. Chem. Soc. Japan, 1935, **56**, 842—851).—The viscosities of gum acacia and gelatin sols and of aq. Na stearate are diminished by the action of supersonic waves. This is attributed to a change in the micellar structure or in the degree of hydration. Ch. Abs. (*e*)

Electric double layer and the stability of lyophobic colloids. E. J. W. Verwey (Chem. Rev., 1935, **16**, 363—415).—A review. Ch. Abs. (*e*)

Coagulation of sols of mercuric sulphide in alcohol. K. Volkov and J. Glasman (Bull. Sci. Univ. Kiev, 1935, **1**, 85—94).—The particles have a negative charge, the magnitude of which is characteristic of lyophobic colloids. The sol is irreversibly coagulated by $AgNO_3$ or $CuCl_2$, probably due to formation of a surface layer of insol., undissociated mols. Progressive addition of $AlCl_3$ or $FeCl_3$ causes coagulation, followed by peptisation, which is ascribed to the adsorption of solvated mols.; the optimum coagulative concns. of undissociated salts ($HgCl_2$, HgI_2) cannot, however, be explained in this manner. R. T.

Electrolytic coagulation of Prussian-blue sols. E. L. Lederer (Kolloid-Z., 1936, **76**, 54—60).—The coagulation of Prussian-blue sols by a wide range of electrolytes, including uni-, bi-, and tervalent ions, is in accordance with Ostwald's rule. The sols also conform to the requirements of Burton's rule. E. S. H.

Dynamics of colloidal sols. H. R. Kruyt (Natuurwetensch. Tijds., 1936, **18**, 87—88).—A brief review. D. R. D.

Dielectric constant of lyophylic colloids. J. T. G. Overbeek (Natuurwetensch. Tijds., 1936, **18**, 113—117).—ϵ has been determined (with $\nu=3{\cdot}5\times10^8$) for starch, agar, arabinate, gelatin, and ovalbumin sols and gels. It is practically unchanged by gelation, alterations in p_H, or the addition of luteo-$CoCl_3$. It falls slightly on coacervation and shows an unexplained slight increase over the calc. val. at higher temp. (43°). S. C.

Effect of electrolytes on negatively charged silver iodide sols considered in conjunction with micro-cataphoresis [experiments]. F. Bosch and H. Haemers (Natuurwetensch. Tijds., 1936, **18**, 90—103).—Flocculation and cataphoresis experiments with HNO_3, KNO_3, $Ba(NO_3)_2$, $Al(NO_3)_3$, $Th(NO_3)_4$, and mixtures of these electrolytes are described. The results do not show whether discharge by $Th(NO_3)_4$ is due to Th^{IV} or $Th(OH)_4$. S. C.

Velocity of cataphoresis and electrical conductivity of colloids. A. J. Rutgers and J. T. G.

Overbeek (Natuurwetensch. Tijds., 1936, **18**, 88—89).—The differences in the charge on colloid particles as measured by cataphoresis and conductivity measurements are explained by assuming that the particle consists of a central nucleus with a charge $(n+n')e$, surrounded by a firmly attached H_2O layer (Smoluchowski), charge $-n'e$, in which the ions move freely with regard to the H_2O, and a diffuse layer, charge $-ne$. S. C.

Sensitisation and protective action of starch on negative sols. M. de Smet (Natuurwetensch. Tijds., 1936, **18**, 118—122).—In order to explain the clarification of coal-washing liquors by adding starch (I), NaOH, and $Ca(OH)_2$, the action of (I) and electrolytes on negative C and AgI sols has been studied. Small amounts ($<10^{-4}\%$) of a hydrophilic colloid make a negatively charged hydrophobic colloid much more sensitive to electrolytes, but larger amounts have a stabilising effect. This adequately explains the action of (I) and $Ca(OH)_2$, but the action of NaOH is still obscure. No theoretical explanation of the phenomena is forthcoming. S. C.

Composition and ionic exchange of ferric silicates and phosphates. A. J. Pugh and M. S. du Toit (Soil Sci., 1936, **41**, 417—431).—The composition and exchange reactions have been examined in relation to p_{H}. The colloidal condition of these complexes is attained by a continuous process of polymerisation with formation of covalent compounds, until the unit forms a micelle of colloidal dimensions. The dissociation of the complex forms the basis of exchange reactions, the mechanism of which is discussed. A. G. P.

Chemical activity of silicic acid. V. N. Krestinskaja and O. S. Moltschanova (Kolloid-Z., 1936, **76**, 60—72).—When $CuSO_4$ is added to sols of SiO_2 or Na_2SiO_3 solutions, Cu and Na are exchanged in equiv. amounts; with SiO_2 sols the action of $CuSO_4$ depends on the $Na^{\cdot}$ content of the sol. Potentiometric titration curves of SiO_2 sols and Na_2SiO_3 solutions with H_2SO_4 are discussed. E. S. H.

Gels of aluminium bromide with nitromethane. J. P. Meshenni (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 85—87).—$MeNO_2$ and $AlBr_3$ yield a gel, which gradually liquefies when exposed to the air, and decomposes to yield an emulsion of $MeNO_2$ when immersed in H_2O. R. T.

Gelatinised emulsions. II. Influence of electrolytes on the emulsifying power of alkali soaps. L. Kremnev and T. Papkova-Kvitzel (Acta Physicochim. U.R.S.S., 1935, **3**, 451—464; cf. this vol., 158).—The emulsifying power of alkali soaps is increased by the addition of small concns. of electrolytes. This is ascribed to the influence of the latter on the hydrolysis of the soaps, and is not observed on the addition of glucose. High concns. of electrolytes cause a marked decrease in emulsifying power, which is correlated with the degree of hydration of the added ions. Addition of glucose causes a decrease in emulsifying power. O. D. S.

Emeraldin sols. II. Mechanism of stabilising effect of gelatin in the production of sols. V. Pschelin (Kolloid-Z., 1936, **76**, 72—81; cf. A., 1935, 580).—A min. amount of gelatin is required for the stabilisation of emeraldin sols, the amount depending on the conditions of prep. of the sol. When an incompletely protected sol is coagulated, all the gelatin is found in the ppt. The mechanism of stabilisation and protection is discussed. E. S. H.

Influence of hydrogen-ion concentration on gelatin. R. Reiger and S. Bach (Kolloid-Z., 1936, **76**, 82—83).—The time of gelation of gelatin is uninfluenced by $[H^{\cdot}]$ between p_{H} 4·05 and 7·8. E. S. H.

Thixotropic gelation. I. Mechanism of thixotropic gelation. J. L. Russell and E. K. Rideal. **II. Coagulation of clay suspensions.** J. L. Russell (Proc. Roy. Soc., 1936, A, **154**, 540—549, 550—560).—I. Small amounts of Al_2O_3 added to SiO_2 suspensions produce thixotropic gels. Gelation is caused by as little as 1 part of Al_2O_3 to 4000 parts of relatively coarse quartz particles. The increase in vol. of the gel $\propto$ the wt. of Al_2O_3 added with larger wts. of Al_2O_3. The results support the theory that thixotropic gelation is due to the oriented coagulation of the colloid.

II. Moderately conc. clay suspensions show three types of coagulation, depending on the electrolyte concn.; at low concn. there is a partial flocculation of a lyophobic nature, at medium concn. a thixotropic gelation, and at high concn. a complete flocculation of a hydrophilic nature. The properties of the suspensions show that the clay consists partly of a highly disperse gel-forming material, and partly of a coarser material with no capacity for gelation. The apparent viscosity of the thixotropic clay gels varies inversely as the cube of the applied stress. The gels show a well-defined breaking point when stretched beyond a certain limit, and no permanent rigidity at low stresses. L. L. B.

Mechanism of the movement of ions of chlorine and hydrogen in the presence of gelatin. S. A. Schtschukarev and V. M. Vdovenko (J. Phys. Chem. U.S.S.R., 1934, **5**, 512—520).—Vals. for the sp. conductivity, relative η, and transport nos. of $H^{\cdot}$ and Cl' for 0·1*N*-HCl in 0—10% gelatin at 40° are recorded. The mobility of Cl' passes through a max. with increasing gelatin concn., whereas that of $H^{\cdot}$ falls continuously. A loose linking between $H^{\cdot}$ and gelatin is assumed, which reduces the effective $[H^{\cdot}]$. The gelatin also increases η and so decreases the mobility of both Cl' and $H^{\cdot}$. Ch. Abs. (*e*)

Electrokinetic phenomena. XII. Electro-osmotic and electrophoretic mobilities of protein surfaces in dilute salt solutions. L. S. Moyer and H. A. Abramson (J. Gen. Physiol., 1936, **19**, 727—738).—The ratio of the two mobilities of protein-coated surfaces (quartz, Pyrex, or paraffin coated with gelatin) is approx. 1·0. H. G. R.

Effect of denaturation on the colloidal behaviour of ovalbumin. P. Koets and J. Schoofs (Natuurwetensch. Tijds., 1936, **18**, 103—106).—Observations on the coacervation and flocculation

of normal and denatured ovalbumin (I) on the addition of Na arabinate sols, as well as measurements of electrocataphoresis, show that during the denaturing process (heating to 100°) no change takes place in the density of the charge on (I) but that the sol changes in character from hydrophilic to hydrophobic.
S. C.

Thermodynamic equations at the absolute zero. V. A. Plotnikov (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 37—44).—Theoretical. R. T.

Inner thermodynamics. II. V. Njegovan (Acta phys. polon., 1934, **3**, 213—214; Chem. Zentr., 1935, ii, 2930).—Theoretical. J. S. A.

Thermodynamics of intermediate reactions. H. Schmid (Z. Elektrochem., 1936, **42**, 579).—Theoretical. E. S. H.

Inversion of the ammonia equilibrium. E. N. Eremin and N. I. Kobosev (Acta Physicochim. U.R.S.S., 1935, **3**, 151—160).—The inversion of the $N_2+3H_2 \rightleftharpoons 2NH_3$ equilibrium at high temp. noted by Maxted is connected with the thermal dissociation of H_2. The inversion temp. corresponds with that at which the dissociation of H_2 becomes marked. At. H combines readily with N_2 at 1000—1500° abs. The problem is treated quantitatively and the results agree well with experiment. A. J. M.

Nomogram for the formation of ammonia in the equilibrium reaction $2NH_3 \rightleftharpoons 3H_2 + N_2$. P. Montagne (Bull. Soc. chim., 1936, [v], 3, 1424—1427).
E. S. H.

Limiting high-temperature rotational partition function of non-rigid molecules. IV. Ethylene, propylene, Δ^α-butene, *cis*- and *trans*-Δ^β-butene, *iso*butene, trimethylethylene, tetramethylethylene, and butadiene. V. Equilibrium constants for reactions of paraffins, olefines, and hydrogen. L. S. Kassel (J. Chem. Physics, 1936, **4**, 435—441; cf. this vol., 673).—IV. Data are calc. and compared with experimental vals.

V. Equilibrium consts. for the dehydrogenation of C_2H_6, C_3H_8, and *n*- and *iso*-C_4H_{10} are calc. on the basis of vibrational frequency data, and compared with experimental vals. The discrepancies are discussed. Equilibrium consts. for the reactions $2C_2H_4=C_4H_8$, $CH_4+C_2H_4=C_3H_8$, $CH_4+C_3H_6=C_4H_{10}$, and $C_2H_6+C_2H_4=C_4H_{10}$ are also calc. H. J. E.

Dissociation relations of the water HOD. I. H. Erlenmeyer and A. Epprecht (Helv. Chim. Acta, 1936, **19**, 677—680).—From previous data [H˙] and [D˙] in pure HOD are calc. to be 0·564 and $0{\cdot}111\times10^{-7}$, respectively. T. G. P.

Extremely weak acids. W. K. McEwen (J. Amer. Chem. Soc., 1936, **58**, 1124—1129).—The acidity of 30 compounds (arylated hydrocarbons, alcohols, enols, amines) is determined by three different methods: (i) colorimetric; essentially that of Conant and Wheland (A., 1932, 572); (ii) spectroscopic; the compound is titrated with $CNaPh_3$ in an inert atm. using ætioporphyrin I as indicator; (iii) polarimetric; the compound is treated with Na *l*-menthoxide and the position of equilibrium determined. The *pK* vals. are tabulated. tert.-*Butyl-fluorene*, m.p. 61°, is obtained by reduction (red P, HI, AcOH) of the -fluorenol. H. B.

Relation between the dissociation constants of substituted aliphatic acids and the distance between the dissociating and the substituted groups. J. P. Greenstein (J. Amer. Chem. Soc., 1936, **58**, 1314—1316).—An inverse linear relation exists between *pK* and l^2 (the square of the distance, in A., from the centre of the dipole group to the carboxyl centre on the assumption of an extended chain), when l^2 is substituted for *d* in MacInnes' equation (A., 1928, 1326). For αβ substitution l^2 is about twice, and for a γ substitution about three times, that for an α substitution. E. S. H.

Dissociation constants of ascorbic acid and its iodine oxidation product. G. Carpéni (Compt. rend., 1936, **203**, 75—78).—Dissociation consts. of ascorbic acid obtained electrometrically are 2×10^{-5} and $6{\cdot}3\times10^{-13}$ at 1°, and $6{\cdot}76\times10^{-5}$ and $2{\cdot}75\times10^{-12}$ at 20°. If the oxidation product, oxyascorbic acid, is titrated rapidly with NaOH, without waiting for equilibrium to be attained, the const. obtained is $2{\cdot}4\times10^{-9}$ at 20°, but a return titration with HCl gives a new curve indicating two consts., $8{\cdot}9\times10^{-4}$ and $1{\cdot}6\times10^{-5}$. Slow titration with NaOH indicates three consts., 6×10^{-4}, $1{\cdot}2\times10^{-8}$, and $5{\cdot}1\times10^{-11}$, whilst the return titration indicates $1{\cdot}8\times10^{-3}$, $7{\cdot}1\times10^{-5}$, and $3{\cdot}2\times10^{-9}$. C. R. H.

Activity coefficients of ions. (Mlle.) M. Quintin (J. Chim. phys., 1936, **33**, 433—447).—Full details are given of work previously reported (this vol., 289). From e.m.f. data for $CuSO_4$, the calc. radii (Debye *a*) of Cu^{++} and SO_4^{--} are $3{\cdot}5\pm0{\cdot}2$ and 1·3 A., respectively. J. G. A. G.

Thermodynamics of liquid–vapour equilibrium in system nitrogen–oxygen. I. R. Kritschevski and N. S. Torotscheschnikov (Z. physikal. Chem., 1936, **176**, 338—346).—The fugacity, *f*, of N_2 has been calc. at 100—125° abs. and 2·5—32 atm. from *p*–*v*–*T* and from thermal data; the two methods yield concordant results. For N_2 in the vapour in equilibrium with a liquid N_2–O_2 mixture *f* is equal to the product of the mol. fraction of N_2 in the liquid and the fugacity of pure N_2 under a pressure equal to the total v.p. of the mixture. *f* for the O_2 must obey a similar law. R. C.

Vapour pressure measurements of the system calcium chloride–water. A. Lannung (Z. anorg. Chem., 1936, **228**, 1—18).—Measurements made with a hot-wire manometer (cf. A., 1934, 1170) at 0—50° are recorded. The dihydrate exists in two forms. Basset's observations on the tetrahydrate are confirmed (cf. A., 1933, 352). Heats of linking of the separate H_2O mols. in the hydrates are calc.
H. J. E.

Vapour pressures of saturated aqueous solutions. Mono- and di-ammonium hydrogen phosphates. E. J. Roehl (J. Amer. Chem. Soc., 1936, **58**, 1291—1292).—For $NH_4H_2PO_4$ at 19—90° the results are given by $\log P= -2240/T+8{\cdot}862$, and for $(NH_4)_2HPO_4$ at 19—55° by $\log P= -2240/T+8{\cdot}807$, with mean deviations of 0·8% and 0·4%, respectively. These and previous data for other saturated aq. solutions show a linear relation between log *P* and 1/*T*, which when plotted gives lines parallel to that for H_2O. E. S. H.

Heavy water of crystallisation. J. R. Partington and K. Stratton (Nature, 1936, **137**, 1075—1076).—The dissociation pressure of $CuSO_4,5D_2O$ is 6·655 mm. at 25° and 9·285 mm. at 30°. If the reaction is $CuSO_4,5D_2O \rightleftharpoons CuSO_4,3D_2O+2D_2O$, this gives 4437 g.-cal. for the heat of combination of $2D_2O_{liq.}$, the corresponding val. for $2H_2O$ being 5560 g.-cal. L. S. T.

System albite–fayalite. N. L. Bowen and J. F. Schairer (Proc. Nat. Acad. Sci., 1936, **22**, 345—350).—F.p. and m.p. are recorded for the entire range of mixtures. The eutectic, m.p. 1050°±5°, contains 84% of albite (I), and the liquidus of (I) is a straight line. J. G. A. G.

Representation of ternary systems. E. Scheil (Arch. Eisenhüttenw., 1935—6, **9**, 571—573).—To assist in understanding ternary diagrams it is recommended that the interrelationships of the 3- and 4-phase equilibria be summarised in a tabular form; examples of these are given for numerous Fe systems. A. R. P.

Ternary systems $KI–K_2SO_4–H_2O$ and $NaI–Na_2SO_4–H_2O$. J. E. Ricci (J. Amer. Chem. Soc., 1936, **58**. 1077—1079).—Equilibrium data are given for $KI–K_2SO_4–H_2O$ at 25° and for $NaI–Na_2SO_4–H_2O$ at 15°, 25°, and 45°. No double salts or solid solutions are formed. E. S. H.

Phase-rule study of the calcium arsenates, G. W. Pearce and L. B. Norton (J. Amer. Chem. Soc., 1936, **58**, 1104—1108).—Study of the system $CaO–As_2O_5–H_2O$ at 90° shows the existence of $CaHAsO_4$, $Ca_5H_2(AsO_4)_4$, $Ca_3(AsO_4)_2$, and $3Ca_3(AsO_4)_2,Ca(OH)_2$. E. S. H.

Equilibria in the system $Li_2O–SiO_2–CO_2$. C. Kröger and E. Fingas (Festschr. Tech. Hochschule Breslau, 1935, 296—306; Chem. Zentr., 1935, ii, 2793; cf. A., 1933, 916).—The equilibrium state resulting from the action of SiO_2 on Li_2CO_3 has been studied. J. S. A.

Equilibrium diagrams of salts for salt baths. V. System $BaCl_2–CaCl_2–KCl$. T. Satô and T. Amano (Kinz-no-Kenk., 1934, **11**, 549—560; cf. A., 1935, 303).—In the system $CaCl_2–KCl$ the *compound* $CaCl_2,KCl$ (m.p. 760°) is formed. This forms eutectics with KCl and $CaCl_2$ at 655° (25 mol.-% KCl) and 615° (76 mol.-% KCl), respectively. The ternary eutectics are at 543°, 553°, and 552° ($BaCl_2$ 23, 26, 21, $CaCl_2$ 58, 18, 17, KCl 19, 56, 62 mol.-%, respectively). Ch. Abs. (*e*)

Systems zirconium oxalate–alkali oxalates–water. (Mlle.) J. Boulanger (Compt. rend., 1936, **203**, 87—90).—The following solid phases were obtained: $3Na_2X,2ZrOX,H_2X,8H_2O$; $2Na_2X,ZrOX,H_2X,2H_2O$; $2(NH_4)_2X,ZrOX,H_2X,2H_2O$; $2Li_2X,ZrOX,H_2X,7H_2O$ ($X=C_2O_4$). C. R. H.

Equilibrium in the reaction of hydrogen with ferrous oxide in liquid iron at 1600°. M. G. Fontana and J. Chipman (Trans. Amer. Soc. Metals, 1936, **24**, 313—332).—An error in previous work is shown to be due to concn. gradients in the gas caused by temp. gradients. The present work shows that the equilibrium const. *K* is 4·75 and is independent of [O], and the activity of FeO dissolved in liquid Fe ∝ its wt.-%. The free energy of formation of FeO in 1% solution is −34,740 g.-cal. at 1600°. The val. of *K* for the $C+FeO \rightleftharpoons Fe+CO$ reaction is calc. to be 0·006, in good agreement with the experimental val. 0·010 previously obtained. W. P. R.

Equilibrium between iron and nickel and their silicates saturated with silicic acid. P. Bardenheuer and E. Brauns (Mitt. Kaiser-Wilh.-Inst. Eisenforsch., 1935, **17**, 127—132; Chem. Zentr., 1935, ii, 2872).—Equilibrium data at 1600° are recorded. H. J. E.

Equilibrium between niobium pentoxide, sodium carbonate, and carbon dioxide. P. Süe (Compt. rend., 1936, **203**, 90—92).—The reactions $Nb_2O_5+Na_2CO_3$ and $NaNbO_3+Na_2CO_3$ have been studied by measuring the equilibrium pressure of CO_2 liberated. The heats of reaction are, respectively, 25 and 91·5 kg.-cal. C. R. H.

Systems $CaO–Al_2O_3–CaCl_2–H_2O$ and $CaO–SiO_2–CaCl_2–H_2O$. R. Nacken and R. Mosebach (Z. anorg. Chem., 1936, **228**, 19—27; cf. B., 1935, 1096).—Aq. $CaCl_2$ reacts fairly rapidly with $3CaO,Al_2O_3$ at 30°, forming the *compound* $3CaO,Al_2O_3,CaCl_2,10H_2O$. Solubility data are given. This reaction controls the influence of $CaCl_2$ on the setting of Portland cement. No corresponding compound is formed from $3CaO,SiO_2$ and aq. $CaCl_2$. The $CaCl_2$ retards the reaction between $3CaO,SiO_2$ and H_2O. H. J. E.

Thermal equilibrium in ternary systems. XIII. Tetramorphism of ammonium nitrate in the ternary system with carbamide and resorcinol. K. Hrynakowski and M. Szmytówna (Rocz. Chem., 1936, **16**, 181—186).—The fusion diagram has been constructed. The transition points for the various polymorphs of NH_4NO_3 are the same as for the pure salt. R. T.

Free energy of dissociation of hydrogen. E. N. Eremin (Acta Physicochim. U.R.S.S., 1935, **3**, 147—150).—The spectroscopic val. for the heat capacity of H_2 and the experimental vals. of the heat of dissociation are used in deriving an equation for the free energy of dissociation of H_2. The equilibrium consts. of the dissociation calc. from the equation for different temp. are in good agreement with the vals. obtained by Giauque. A. J. M.

Determination of heats of dissolution [of silicates] in acids of various concentration. H. E. Schwiete and A. Pranschke (Zement, 1935, **24**, 593—598; Chem. Zentr., 1935, ii, 2931).—With a large excess of acid, the heat of dissolution changes only by an amount which corresponds with the heat of dilution of the acid. The heat of hydration of CaO is determined as 15 kg.-cal. per mol. J. S. A.

Molecular conductivity of strong electrolytes in concentrated solutions. S. Kaneko (J. Chem. Soc. Japan, 1935, **56**, 793—795).—A formula is derived for the mol. conductivity of binary salts of equal ionic valency. For KCl it is valid up to 1*N*. Ch. Abs. (*e*)

Electric conductivity and viscosity of salts dissolved in solutions of carbohydrates and glycerol. J. Dědek and J. Dykyj (Coll. Czech. Chem. Comm., 1936, 8, 261—287).—The data refer to aq. solutions at 20—50° containing 0—88 g. of sucrose, glucose, and glycerol per 100 c.c. of solution and 0·001—1·0N concns. of electrolyte. The relation $1/\Lambda_v\eta = ax+b$, where Λ_v is the equiv. conductivity at dilution v and η is the viscosity of the aq. non-electrolyte (x g. per 100 c.c. of solution) and a and b are consts., applies, in general, when x is >30, and, in some cases when x is >0. With Cl′ as anion, a and b increase for the cations in the order $H^{\cdot}<K^{\cdot}<Na^{\cdot}<Li^{\cdot}$. With const. [KCl], the order of the vals. of a and b is glycerol<glucose<sucrose, but with rise of temp., a decreases (becomes less negative) and b increases. a and b decrease as v increases. The relation of these results to the rules of Walden and Johnston is discussed. J. G. A. G.

Influence of pressure on conductivity of solutions. P. Z. Fischer (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 303—307).—A review. R. T.

Effect of non-electrolytes on the conductivity of electrolyte solutions. V. A. Plotnikov, P. Z. Fischer, and V. P. Barabanov (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 211—226).—The sp. conductivity of 0·33—3·83N-KCl, 0·5—2·5N-KNO_3, and 0·3—4·94N-$AgNO_3$ in presence of $CO(NH_2)_2$ (19 and 35%), mannitol (3—9%), or sucrose (5—50%) shows no obvious connexion with the viscosity; the formation of dissociable non-electrolyte–electrolyte complexes is postulated. R. T.

Influence of non-electrolytes on conductivity of aqueous electrolytes. K. Volkov and A. Almazov (Bull. Sci. Univ. Kiev, 1935, 1, 191—205).—The conductivity (κ) and η of aq. KCl–dextrin (I) or sol. starch (II) do not run parallel. With const. concn. of (I) or (II), the % diminution in κ rises to a max. at 0·03—0·5N-KCl, thereafter steadily falling with further rise in [KCl], whilst when the relative concns. of (I) and KCl are maintained const. but the total concn. is progressively increased, κ rises asymptotically to a const. val. It is inferred that aq. (I) and (II) have a discontinuous structure, and that the effects are not due to dehydration of ions by the added colloids. R. T.

Electrochemistry of ternary systems in solvents of low dielectric constant. E. J. Gorenbein (Bull. Sci. Univ. Kiev, 1935, 1, 101—129).—Sp. conductivity in the systems $AlBr_3$–MBr–solvent (M=Li, K, Rb, Cu, Ag; solvent=C_6H_6, PhMe, $C_2H_4Br_2$, EtBr) rises with increase in the dielectric const. of the solvent. In systems containing Li, K, or Rb, Al is deposited at the cathode during electrolysis. R. T.

(A) **Compounds of aluminium bromide with lithium, copper, and silver bromide.** (B) **Electrochemical study of the systems $AlBr_3$–$SbBr_3$ in toluene,** (C) **$AlBr_3$–$BiBr_3$ in benzene,** (D) **aluminium bromide–silver and copper halides–organic solvents (ethyl bromide, ethylene dibromide, benzene).** V. A. Plotnikov (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 3—9, 227—233, 235—244; 1936, 3, 89—109).—(A) [with E. J. Gorenbein]. Conductivity in the systems $AlBr_3$–EtBr–LiBr, –CuBr, and –AgBr is ascribed to the *compounds* LiBr,$AlBr_3$, m.p. 192°, CuBr,$AlBr_3$, m.p. 241°, and 2AgBr,3$AlBr_3$, m.p. 180—185°. Stability of the compounds towards H_2O falls in the order given.

(B) [with V. A. Kiketz and P. A. Radomski]. Max. sp. conductivity κ is found for mixtures in which Sb : Al = 1 : 2, suggesting the compound $SbBr_3$,2$AlBr_3$. The decomp. potential (18°) is 0·9 volt, Sb being deposited at the cathode.

(C) [with V. A. Kiketz and L. A. Korol]. The κ–composition curve has a max. corresponding with the compound 2$BiBr_3$,2$AlBr_3$. Electrolysis with a Bi anode leads to deposition of Bi in accordance with Faraday's law (decomp. potential 0·9 volt).

(D) [with E. J. Gorenbein]. The value of κ rises in the systems $AlBr_3$–MX–EtBr, –$C_2H_4Br_2$, or –C_6H_6 (M=Cu, Ag; X=Cl, Br, I) with increasing [MX]; no obvious connexion exists between dipole moment of solvent and κ. Cu or Ag is deposited in theoretical yield at the cathode. Decomp. potentials are recorded. R. T.

Measurement of conductivity of fused salts, and conductivity in the system NaCl–$CaCl_2$. V. Barzakovski (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 153—158).—Apparatus for determining the conductivity (c) of fused salts is described. The c–composition curves at 700—1000° have a min., and the temp. coeff. of c–composition curves a max., at 70—80 mol.-% of $CaCl_2$; c rises with increasing temp. R. T.

Electrolysis of sodium chloride in liquid ammonia. II. E. I. Achumov and N. A. Gontscharov (J. Gen. Chem. Russ., 1936, 6, 534—541; cf. A., 1935, 1080).—Sp. conductivities are recorded for solutions of NaCl, NH_4Cl, and NaCl+NH_4Cl in liquid NH_3, at −34° to 34°; for saturated solutions of NaCl max. κ is at −8·4°. Curves connecting decomp. potential with temp. are given for solutions of NaCl in NH_3 and H_2O. R. T.

(A) **Diffusion of potassium ferrocyanide, ferricyanide, and dichromate, and of sodium, magnesium, potassium, and calcium chloride, and the mobility of the ions of these salts.** (B) **Diffusion coefficient of potassium perrhenate.** S. Pleśniewicz (Rocz. Chem., 1936, 16, 223—240, 241—244).—(A) The diffusion coeffs. D in 0·1N solutions at 20° are: $K_4Fe(CN)_6$ 0·845, $K_3Fe(CN)_6$ 0·917, $K_2Cr_2O_7$ 1·043, NaCl 1·166±0·007, $MgCl_2$ 0·832±0·003, KCl 1·449, $CaCl_2$ 0·896±0·008. D cannot be calc. from Nernst's equation $D=RT/F^2[(1/\nu_k)+(1/\nu_a)]\,.\,u_ku_a/(u_k+u_a)$, since u applies to infinite dilution. The conception of mean transport nos. υ, applying to a given concn. gradient, is introduced, υ_a being equal to $k\upsilon_k$, and $1/D=(F^2/RT)n_kn_a/(n_k+n_a)\,.\,(1/\upsilon_k+1/\upsilon_a)$, where n_a and n_k are the valencies and υ_a and υ_k the mean transport nos. of the anion and cation, respectively, and k and F are consts.

(B) The D of $KReO_4$ (0·01N) at 20° is 1·233, and the υ of ReO_4' at 18° is 44·07. R. T.

Structure of molecules in solution. C. Duval (Document. sci., 1935, 4, 145—148; Chem. Zentr., 1935, ii, 3051).—From observations on electrophoresis and analyses of the contents of the anode and cathode compartments the following structural formulæ are suggested: kainite $[MgSO_4Cl(H_2O)_3]K$; $(CrO_3SO_4)H_2$; $(SO_3SO_4)H_2$; $(CrO_3CrO_4)H_2$; $[Co(CO_3)_3]Co$; $[Co(H_2O)_3Cl_3]H$; $[Co(H_2O)_3Cl_3]_2Co$; $[Co(H_2O)_3Cl_3]Li$. H. J. E.

Solid electrolytes. P. FISCHER (Bull. Sci. Univ. Kiev, 1935, **1**, 131—140).—A review. R. T.

Nomogram for the relation between quinhydrone potential and p_H at various temperatures. G. KNAYSI (Food Res., 1936, **1**, 297—299). E. C. S.

Poisoning of platinum in hydrogen electrodes. H. JABŁCZYŃSKA-JĘDRZEJEWSKA (Rocz. Chem., 1936, **16**, 306—312).—Pt electrodes are poisoned by $0{\cdot}00025N$-H_2S, the potential tending to a const. min. val. of 160 mv., irrespective of the $[H_2S]$. The effect increases with increasing p_H. Reactivation is possible by the successive action of nascent O and H. R. T.

Potentials at the interface of two liquid phases. III. K. KARCZEWSKI (Rocz. Chem., 1936, **16**, 254—258; cf. this vol., 928).—The potential at the interface $Bu^{\beta}OH$–aq. K salt becomes more positive with increasing $[K_2SO_4]$, and less positive in the case of KCl, KBr, KI, KCNS, K_2CO_3, HCO_2K, KNO_3, $KClO_3$, and $KClO_4$. R. T.

Influence of composition of solutions on the electrocapillary curve of mercury. W. KEMULA and E. BEER (Rocz. Chem., 1936, **16**, 259—269).—The electrocapillary curves obtained by the static and dynamic methods coincide in the case of conc. but not dil. solutions. Irregularities in the curves obtained by the dynamic method are ascribed to the influence of the ζ-potential. The results for KCl, $BaCl_2$, and $LaCl_3$ are in agreement with Stern's theory (Z. Elektrochem., 1924, **30**, 508). R. T.

Polarographic studies with the dropping mercury cathode. LIX. Anomalous curves of certain potassium chloride solutions. A. R. WEIR (Coll. Czech. Chem. Comm., 1936, **8**, 239—245).—The current–voltage curves for the electrolysis of aq. KCl saturated with Hg_2Cl_2 are similar to those for NaCl except in solutions containing 45·6—59·5 g. of KCl per 1000 g. of H_2O which give variable curves of anomalous contour. These results are parallel with v.p. anomalies (cf. this vol., 678). J. G. A. G.

Anode polarisation of metallic electrodes. I. Polycrystalline and liquid electrodes. W. TRZEBIATOWSKI and M. SARNOWSKI (Rocz. Chem., 1936, **16**, 187—198).—The polarisation of Cu anodes (0°, 25°, and 50°) in aq. $CuSO_4$–H_2SO_4 varies with the crystal structure of the metal. R. T.

Decomposition potentials of fused salts. V. M. GUSKOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 159—173).—E.m.f. measurements relating to the cell Mg|molten $MgCl_2$|Cl (C anode; molten NaCl–KCl–$MgCl_2$ electrolyte) at 665—793° afford no evidence of the existence of complex anions of the type $MgCl_3'$. The temp. coeff. of the e.m.f. is $0{\cdot}7\times10^{-3}$. The results suggest that cryolite dissociates as follows: $Na_3AlF_6 \rightleftharpoons 3Na^{\cdot}+Al^{\cdot\cdot\cdot}+6F'$, the reaction at the C anode being $2Al_2O_3+3C+6F_2 \rightarrow 4AlF_3+3CO_2$; $CO_2+C \rightarrow 2CO$. R. T.

Decomposition potential of aluminium chloride ammines. V. A. PLOTNIKOV and M. S. FORTUNATOV (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, **2**, 251—256).—N_2 is evolved, in accordance with Faraday's law, at a Pt anode from a molten mixture of $AlCl_3$ ammines. The decomp. potentials vary with temp. and c.d. R. T.

Electrolysis of non-aqueous solutions. V. S. FINKELSCHTEIN (Coll. Trans. 1st. U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 54—71).—Previous explanations of deviations from Faraday's law are not satisfactory. In the system $AsCl_3$–Et_2O the val. of the decomp. potential is affected only by addition of solvents the dipole moment of which is > that of Et_2O. Electrolysis in liquid NH_3 and deposition of Al from non-aq. solvents are discussed. R. T.

Strong oxidising agents in nitric acid solution. I. Oxidation potential of cerous–ceric salts. II. Oxidation potential of thallous–thallic salts. A. A. NOYES and C. S. GARNER (J. Amer. Chem. Soc., 1936, **58**, 1265—1268, 1268—1270).—I. E.m.f. of cells of the type Pt–N_2 (1 atm.)|$HClO_4(c')$, $HNO_3(c)$ $+Ce^{IV}(c_2)+Ce^{III}(c_1)$|Pt at 25° and 0° are recorded. E_0 varies little with considerable change in the Ce^{III}/Ce^{IV} ratio, acid concn., or ionic strength. It follows that nitrate complexes are formed only slightly, if at all, and that a hydrolytic reaction, such as $Ce^{\cdot\cdot\cdot\cdot}+H_2O=CeOH^{\cdot\cdot\cdot}+H^{\cdot}$, does not occur appreciably. The Ce^{III}–Ce^{IV} oxidation potential in HNO_3 is $1{\cdot}6095\pm0{\cdot}0007$ volts at 25° and 1·601 volts at 0°.

II. E.m.f. measurements of cells of the type Pt–H_2 (1 atm.)|$HClO_4(c')$, $HNO_3(c)+Tl^{III}(c_2)+Tl^{I}(c_1)$|Pt show that the formal oxidation potential of Tl^{III}–Tl^{I} is $1{\cdot}2303\pm0{\cdot}0007$ volts at 25° and $1{\cdot}193\pm0{\cdot}001$ volts at 0° in HNO_3. These vals. remain const. when Tl^{I}/Tl^{III} is varied 100-fold and over a wide range of $[HNO_3]$, showing that hydrolysis of $Tl(NO_3)_3$ or formation of nitrate complexes does not occur appreciably. E. S. H.

Extension of Arrhenius' conception of a chemical reaction. J. A. CHRISTIANSEN (Z. physikal. Chem., 1936, **B**, **33**, 145—155; cf. A., 1935, 707).—Assuming an open sequence of reactions with many or an infinite no. of steps in series with each other, the above concept leads for a unimol. reaction to an expression similar to Nernst's reaction velocity = (chemical force)/(chemical resistance). The force is equal to the difference in activity between the initial and final states of the system and the resistance to an integral which varies with temp. R. C.

Kinetics of gas reactions: an attempt to connect thermal decomposition and oxidation processes. M. W. TRAVERS (Nature, 1936, **138**, 26—27).—The similarity in the curves representing the rate of thermal decomp. and that of oxidation of CH_2O and MeCHO can be accounted for by the formation of short-lived intermediates. L. S. T.

Period of induction in the inflammation of gas mixtures. A. E. MALINOVSKI (Acta Physicochim. U.R.S.S., 1935, **3**, 509—516).—Induction periods of chain reactions (*a*) when the no. of active centres generated in unit time is const. throughout the reaction, and (*b*) when no active centres are generated after the commencement of the reaction, are calc. O. D. S.

Kinetics of simultaneous polymerisation and ring formation. M. Stoll (Trans. Faraday Soc., 1936, **32**, 1031—1033).—A criticism of the work of Salomon (cf. this vol., 296). O. J. W.

Forjaz's effect. L. Rosenkevitsch (Acta Physicochim. U.R.S.S., 1935, **3**, 161—162).—The accelerating effect of a powerful alternating field on the reaction between EtOH and AcOH noted by Forjaz (A., 1934, 40) is attributed to the heating effect of the field. A. J. M.

Oxidation of hypophosphorous acid by iodine in aqueous sulphuric acid. J. Kamecki (Rocz. Chem., 1936, **16**, 199—206).—The velocity of oxidation of H_3PO_2 to H_3PO_3 by (I) rises with increasing $[H_2SO_4]$ to 1·0*N*, thereafter remaining const. Oxidation of H_3PO_3 proceeds slowly. H_3PO_2 is determined in presence of H_3PO_3 by determining the latter in one sample, by the method of Wolf and Jung (A., 1932, 135), adding H_2SO_4 to 1—2*N* and a small excess of I to another sample, and titrating excess of I after 2·5 hr. at 20° (in the dark). R. T.

Kinetics of the tervalent vanadium–iodine reaction. J. B. Ramsey and M. J. Heldman (J. Amer. Chem. Soc., 1936, **58**, 1153—1157).—At 24·95° the reaction in $HClO_4$, at const. ionic strength, is $\propto$ $[I_3']$ and $[V^{\cdots}]$, and inversely $\propto$ $[H^{\cdot}]$ and $[I']$. The rate-determining step is probably bimol., between I mols. and $VOH^{\cdot\cdot}$. The salt effect has been determined and an explanation for its large negative magnitude is advanced. E. S. H.

Kinetics of the nitrite–iodine reaction. G. G. Durrant, R. O. Griffith, and A. McKeown (Trans. Faraday Soc., 1936, **32**, 999—1013).—The kinetics of the reaction between $NaNO_2$ (and KNO_2) and I have been investigated in phosphate buffers at 40°, 50°, and 60°. The reaction rate is given by an equation, which can be explained by a mechanism involving NO_2 and I atoms as intermediaries. This mechanism is supported by results of experiments in which nitrite and oxalate react simultaneously with I. O. J. W.

Speed of decomposition of chromic acid in hot aqueous solutions of sulphur trioxide, and relation between this reaction and oxidising power. H. C. S. Snethlage (Rec. trav. chim., 1936, **55**, 712—722).—The rate of decomp., yielding O_2, has been determined in aq. H_2SO_4 at 138° and in SO_3–H_2SO_4 mixtures at 100°. There occur simultaneously (1) a pseudo-unimol. reaction of the CrO_3 with SO_3 or $H_2S_2O_7$, giving Cr_2O_3, and (2) a bimol. reaction, possibly $2CrO_3=Cr_2O_3+3O$. As the H_2SO_4 concn., *c*, rises above 60% the velocity passes through a max. (81%), then a min. (96—98%), and finally rises rapidly; below 60% there is no measurable decomp. The velocity coeff. of (1), k_1, rises slowly with *c* up to ~99%, then much more rapidly, corresponding with the appearance in the solvent of $H_2S_2O_7$. With (2) the velocity coeff., k_2, rises with *c* up to 81%, then falls up to 99%. The relation of k_1 and k_2 to *c*, however, varies somewhat with $[CrO_3]$. These results explain the data obtained (A., 1935, 1140) for the oxidation of org. substances with CrO_3–H_2SO_4 mixtures; the oxidising power of the latter is probably governed by (2). R. C.

Rate of reaction of sodium sulphite with oxygen dissolved in water. R. M. Hitchens and R. W. Towne (Amer. Soc. Test. Mat., Preprint, June, 1936, 8 pp.).—The reaction proceeds with great rapidity and is complete in <1 min. at temp. approaching 100°, regardless of the type of H_2O, if a slight excess of Na_2SO_3 is employed. A 20% excess of Na_2SO_3 doubles the reaction rate and a 100% excess almost quadruples it. R. B. C.

Kinetics of hydrolysis of esters in alkaline media. V. A. Goltzschmidt, N. K. Vorobjev, and I. V. Potanov (J. Gen. Chem. Russ., 1936, **6**, 757—763).—The velocity coeffs. *k* of hydrolysis by aq. NaOH of a no. of esters, $R\cdot CO_2R'$, at 10°, 20°, and 30° fall with increase in the no. of C atoms in R and R′; for a given R, $k_{Et}/k_{Me}=0\cdot57$, $k_{Pr}/k_{Et}=0\cdot84$, and $k_{Bu}/k_{Pr}=0\cdot93$, but for a given R′, $k_{Et}/k_{Me}=0\cdot84$, and $k_{Pr}/k_{Et}=0\cdot62$. It is concluded that the activity coeff. and the energy of activation both fall with increase in mol. wt. of the ester. R. T.

Rates of esterification of alcohols in formic and acetic acids and of formic acid in *tert*.-butyl alcohol. A. Kailan and S. Rosenblatt (Monatsh., 1936, **68**, 109—170).—The rate of esterification of menthol, borneol, *cyclo*hexanol, α-chloropropan-β-ol, ethylene chloro-, bromo-, and iodo-hydrin, βγ-dichloro-, βγ-dibromo-, βγ-di-iodo-, and β-chloro-*n*-propyl alcohol was studied at 15° and 25° in AcOH and HCO_2H, with and without addition of HCl, and with varied initial $[H_2O]$. The rate in AcOH containing HCl was increased on increasing the $[H_2O]$. In absence of HCl, or in HCO_2H, it was reduced. The increase in rate due to HCl was $\propto$ its concn. The rate of esterification decreases as the no. of halogen atoms in the mol. is increased. Replacement of one six-membered by two five-membered rings increases the rate. H. J. E.

Effect of pressure up to 12,000 kg. per sq. cm. on reactions in solution. E. G. Williams, M. W. Perrin, and R. O. Gibson (Proc. Roy. Soc., 1936, A, **154**, 684—703).—Velocity coeffs. have been measured, by means of the apparatus previously described (A., 1935, 1082), for the following reactions: the interaction of NaOEt and EtI in EtOH solution, between 15° and 30° at 5000, 8500, and 12,000 kg. per sq. cm.; the hydrolysis of $CH_2Cl\cdot CO_2Na$ by aq. NaOH, between 40° and 80° at 1, 3000, 7600, and 12,000 kg. per sq. cm.; the esterification of Ac_2O by EtOH in EtOH solutions, between 15° and 40° at 1, 1000, 2000, and 3000 kg. per sq. cm., and in PhMe, $COMe_2$, C_6H_{14}, and amyl ether solutions, at various temp. at 1 and 3000 kg. per sq. cm.; the decomp. of phenylbenzylmethylallylammonium bromide (I) in $CHCl_3$ between 25° and 45° at 1 and 3000 kg. per sq. cm. In each case the temp. coeffs. of the reactions were measured, in an attempt to show whether the change in the velocity coeff. is due to a change in the const. *A* or *E* in the Arrhenius equation.

The reactions fall into three classes. (1) "Normal" reactions, where pressure has a small accelerating effect which falls at high pressures, the increase in velocity being of the order of 5 times at 12,000 kg. per sq. cm. The acceleration is due chiefly to a decrease in the activation energy. (2) "Slow" reactions, where pressure has a greater accelerating influence which increases with rise of pressure, the increase in velocity being of the order of 10 times at 5000 kg. per sq. cm., and 45 times at 8500 kg. per sq. cm. The consts. A and E of the Arrhenius equation both increase with rise of pressure. (3) Unimol. decomps. The decomp. of (I) in $CHCl_3$ solution is retarded 1·5 times at 3000 kg. per sq. cm. The pressure effect on the EtOH and Ac_2O reaction varies with change of solvent, but it is always of the same order of magnitude. L. L. B.

Kinetic study of the hydrolysis and alcoholysis of phenyl acetate. W. A. Waters (J.C.S., 1936, 1014—1023).—The rates of decomp. of PhOAc by EtOH–H_2O mixtures containing HCl have been investigated. The reactions PhOAc+EtOH→ EtOAc+PhOH (1) and PhOAc+H_2O→AcOH+ PhOH (2) proceed simultaneously at comparable rates. The formation of PhOH followed a unimol. course in all experiments and was irreversible, no other aromatic product being formed. This supports the view that carboxylic esters undergo acid hydrolysis and alcoholysis by fission of an alkoxy-group. The crit. increment of activation for both PhOH and AcOH liberation is approx. the same, suggesting that the activated complexes in both (1) and (2) are the same, not involving EtOH or H_2O. Ester hydrolysis in acid solution may be a unimol. reaction occurring between activated ester–proton complexes and normal solvent mols. D. C. J.

Determination of parameters k and n in the differential equation $dx/dt = k(a - x)^n t^{\nu-1}$. Chemical applications. J. M. Gonzalez Barredo (Anal. Fís. Quím., 1935, **33**, 844—853).—Mathematical. The hydrolysis of EtOAc is discussed as an example.

Graphical methods in kinetics. J. L. G. Caamaño (Anal. Fís. Quím., 1936, **34**, 327—330).—Attention is directed to errors in the work of González Barredo (preceding abstract). F. R. G.

Kinetics of bimolecular associations in solution and in the gaseous state. Mechanism of additions to double linkings. IV. A. Wassermann (J. C. S., 1936, 1028—1034; cf. this vol., 685).—The kinetics of the addition of *cyclo*pentadiene to acraldehyde, benzoquinone, α-naphthaquinone, *cyclo*pentadiene–benzoquinone, and *cyclo*pentadiene are measured in C_6H_6 solution, and compared with the kinetics of corresponding syntheses in the gas phase (*ibid.*, 297). The factor in the Arrhenius equation independent of temp. is much < the collision frequency in the gas phase, and it is suggested that this is due to the complicated structure of the reactants. The conclusion is reached that the collision frequency in solution is approx. the same as that in the gas phase both for "normal" and "slow" bimol. reactions. D. C. J.

Reaction of iodoacetate and of iodoacetamide with various thiol groups, with urease, and with yeast preparations. C. V. Smythe (J. Biol. Chem., 1936, **114**, 601—612).—The rates of reaction of $CH_2I\cdot CO_2'$ (I) and $CH_2I\cdot CO\cdot NH_2$ (II) with a no. of substances containing ·SH were in the order: thioglucose > thiosalicylicacid > cysteine > glutathione > thioglycol; in all cases the rate with (II) was > that with (I). Urease was very resistant to inhibition by (I) but quite susceptible to that by (II); NH_2Ac and $CN\cdot CH_2\cdot CO\cdot NH_2$ were ineffective. It is concluded that inactivation of urease by (II) requires that only 0·25—0·5 of the ·SH be destroyed. The inhibition of fermentation of yeast extracts by (I) is more rapid than that by (II). H. D.

Ionisation of amines in alcohol: a possible slow reaction. A. G. Ogston (J.C.S., 1936, 1023—1025).—A quant. investigation of the slow increase in electrical conductivity found when solutions of NH_3 in MeOH and EtOH are diluted is made (cf. A., 1934, 1071). Similar behaviour is found using $NHEt_2$, NH_2Bu^{β}, $CH_2Ph\cdot NH_2$, and piperidine. A rapid change, accounting for 0·66 of the total, occurs in the first 2 min. and then the reaction becomes slow and of the first order. The effect is ascribed to a slow ionic reaction. D. C. J.

Rate of absorption of water by magnesium sulphate. A. S. Mikulinski and R. N. Rubinstein (Z. anorg. Chem., 1936, **228**, 89—91).—The rate of absorption of H_2O by $MgSO_4,H_2O$ (I) and $MgSO_4,2H_2O$ (II) in atm. of 100, 70, and 50% R.H. at 18° was measured. The initial rate is smaller for (I) than for (II). H. J. E.

Derivation of general formula for velocity of crystallisation of sucrose from experimental data. A. Kirov (Sovet. Sach., 1933, No. 9, 30—33).—The crystallisation const. and velocity are calc. from the formula $\Delta p = K\Delta C/\eta$ (C=concn.; η=viscosity). Ch. Abs. (*e*)

Rate of dissolution of alkali borate glasses. R. L. Müller and C. V. Weinstein (Acta Physicochim. U.R.S.S., 1935, **3**, 465—502; cf. A., 1932, 447).—The rates of dissolution of glasses of formula $B_2O_3+M_2O$, where M is Li, Na, K, Rb, or Cs, have been investigated for a series of compositions between B_4O_6 and $M_2B_4O_7$. For glasses where the molar fraction, q, of $M_2B_4O_7$ is $\not> 0{\cdot}1$ the rate is determined by diffusion and convection. When q is $\not< 0{\cdot}5$ the rate is independent of the rate of stirring of the liquid and has a temp. coeff. of 7—8% per 1°. It is deduced that the rate of dissolution is here determined by a chemical reaction at the solid–liquid interface which begins to be important in the range $0{\cdot}1 < q < 0{\cdot}5$. The formerly observed correlation between the molar conductivity and the rate of dissolution is fortuitous. O. D. S.

Catalytic oxidation effect of complex metallic compounds. XI. Catalytic oxidation in heavy water. K. Yamasaki (Bull. Chem. Soc. Japan, 1936, **11**, 431—433).—The rate of oxidation of pyrogallol, alone or catalysed by complex Co salts, is greater in H_2O than in D_2O. C. R. H.

Kinetics of the oxidation of solutions of sulphurous acid. S. S. Vassiliev, L. I. Kaschtanov, and T. L. Kastorskaia (Acta Physicochim. U.R.S.S., 1935, **3**, 413—434).—The oxidation of aq. SO_2 by air has been studied with and without the addition of 0·01% of $MnSO_4$ as catalyst. For low $[SO_2]$ the rate $\propto [SO_2]$, the catalysed being 7—8 times as fast as the uncatalysed reaction. For high $[SO_2]$ the rate becomes equal to the rate of dissolution of O_2.
O. D. S.

Acid catalysis in liquid ammonia. Kinetics of the ammonolysis of santonin in liquid ammonia in the presence of ammonium salts. A. I. Schattenstein (Acta Physicochim. U.R.S.S., 1935, **3**, 37—52).—The kinetics of the ammonolysis of santonin were investigated polarimetrically. The catalytic effect of NH_2-acids [santonamide, $CO(NH_2)_2$] and of several NH_4 salts was examined. The velocity coeffs. for 0·1*N* solutions of catalysts are in the order: $NH_4Cl > NH_4Br > NH_4NO_3 > NH_4I > NH_4ClO_4$. The parallelism observed between conductivity and thermodynamic activity and catalytic activity in the case of aq. solutions does not hold when the solvent is liquid NH_3. If to the solution of the acid (NH_4 salt) a neutral (Na) salt with the same anion is added, there is a definite increase in the reaction velocity. The proportionality between velocity coeff. and concn. of catalyst is the better the weaker electrolyte is the catalyst. The mechanism of the catalysis is discussed.
A. J. M.

Acid–base catalysis of the mutarotation of glucose in protium oxide–deuterium oxide mixtures. W. H. Hamill and V. K. La Mer (J. Chem. Physics, 1936, **4**, 395—401).—The velocity of the H_2O–D_2O-catalysed reaction $\propto$ the fraction of heavy glucose and depends only indirectly on the $[D_2O]$ in the water. The velocity of the acid ion catalysis varies linearly with $[D_2O]$. The rate of OAc′ catalysis varies linearly with the fraction of D_2O or of AcOD. The decrease in the rate of the H_2O–D_2O-catalysed reaction with increasing $[D_2O]$ arises from a decrease in the entropy of activation and not from an increase in the activation energy.
H. J. E.

Inhibition of chemical reactions. VI. Influence of ether and nitrobenzene on the absorption of ethylene by sulphuric acid. K. C. Bailey and W. E. Calcutt (Sci. Proc. Roy. Dublin Soc., 1936, **21**, 309—315).—Et_2O and $PhNO_2$ inhibit the rate of absorption of C_2H_4 (cf. A., 1932, 1085) in conc. H_2SO_4. Every Et_2O mol. in the surface appears to inhibit equally 4—5 adjacent H_2SO_4 mols. from absorbing the gas. A similar explanation is impossible for $PhNO_2$. When the absorbing surface is constantly renewed the inhibiting effect of Et_2O or $PhNO_2$ is $<$ in a static system, indicating that the inhibitor acts at the gas–liquid interface rather than in the bulk of the liquid.
J. L. D.

Ozone as oxidising catalyst. XI. Ozonisation of aliphatic aldehydes in different solvents and in the gaseous state. E. Briner and A. Lardon (Helv. Chim. Acta, 1936, **19**, 850—857; cf. this vol., 570).—Ozonisation of CH_2O, MeCHO, EtCHO, and PrCHO in the gas phase and in solution in H_2O, CCl_4, or C_6H_{14} has been studied.
T. G. P.

Release of protons and deuterons from organic molecules in general basic catalysis, exemplified by bromination of nitromethane. O. Reitz (Z. physikal. Chem., 1936, **176**, 363—387).—The rates of bromination, *k*, of $MeNO_2$ and $CD_3 \cdot NO_2$ both in pure H_2O and D_2O and in presence of acetate and chloroacetate buffers have been measured at 25° and 35°. *k* falls with increasing D content of the NO_2-compound, linearly at first, but with increasing slowness at the higher D contents. The ratio of *k* for $MeNO_2$ to that for $CD_3 \cdot NO_2$ under the same conditions is 4—7, which is therefore also the ratio of the rate of protolysis to that of deuterolysis, since these are the processes which determine the rate of bromination as a whole. There is, however, no detectable difference between the energies of activation. Substitution of D_2O for H_2O as solvent depresses *k* by $\sim$20%. The ratio of the strength of H_2O as a base to that of D_2O is $\sim$1·6. At 83° the distribution ratio of D between H_2O and $MeNO_2$ is $\sim$0·8. The prep. of $CD_3 \cdot NO_2$ is described.
R. C.

Thermal decomposition of sodium sulphate in presence of silica and kaolin. J. A. Fialkov and S. D. Schargorodski (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, **2**, 269—283).—Decomp. of Na_2SO_4–SiO_2 mixtures commences at 1100°, the velocity of the reaction increasing with rise of temp. and with the degree of dispersion of the SiO_2. It is catalysed by CeO_2, TiO_2, and Fe_2O_3, but not appreciably by Cr_2O_3 and Al_2O_3. At 1200° the greatest decomp. velocity is attained by heating with kaolin, and the least with river sand, kieselguhr and SiO_2 gel being intermediate. Decomp. is greatly accelerated by raising the kaolin content of the mixtures. The products are SO_2 (evolved chiefly during the first hr. of heating) and Na silicates, aluminates, and aluminosilicates. The mass is readily converted by dil. H_2SO_4 into SiO_2 gel and $Al_2(SO_4)_3$.
R. T.

Catalytic oxidation of sodium sulphite in presence of cupriferous charcoal. K. Volkov and D. Strashesko (Bull. Sci. Univ. Kiev, 1935, **1**, 95—99).—The velocity of oxidation of SO_3'' in presence of C–Cu increases with the $[Cu^{\cdot\cdot}]$ of the solution; SO_3'' or SO_4'' are not adsorbed by the C, and the reaction takes place exclusively in the aq. phase.
R. T.

Effect of catalysts and anticatalysts on the kinetics and mechanism of oxidation of sulphur dioxide by ozone. L. I. Kaschtanov and V. P. Rishov (J. Gen. Chem. Russ., 1936, **6**, 732—747).—The stoicheiometric coeff. *a* (no. of mols. of SO_2 oxidised per mol. of O_3) rises with increasing $[SO_2]$ and diminishing $[O_3]$ to a max. of 18; the val. of *a* is unaffected by varying the rate of flow of the gas mixture, by presence of PhOH, alone or with $MnSO_4$, or by presence of benzoquinone, and remains const. at 0—60°. The velocity of reaction increases with rising temp., and falls with increasing $[H_2SO_4]$ in the absorbent solution. The reaction is catalysed by $MnSO_4$. O_3 oxidises PhOH to benzoquinone, and $Mn^{\cdot\cdot}$ to MnO_4', but MnO_4' production is inhibited by PhOH. The application of the above findings to desulphurisation of flue gas, with recovery of H_2SO_4, is discussed.
R. T.

Influence of crystalline addenda on the velocity of evolution of gas from carbonates. II. B. Srebrow (Kolloid-Z., 1936, **76**, 149—153; cf. A., 1935, 942).—The rate of thermal decomp. of $ZnCO_3$ at 254° and of $NiCO_3$ at 330° is increased by adding small amounts of ZnO, MnO_2, FeO, Fe_2O_3, CuO, PbO, or WO_3. E. S. H.

Mechanism of catalytic oxidation of carbon monoxide on manganese dioxide. III. Existence of a critical lower pressure limit in the heterogenous oxidation. F. Charachorin, S. Elovitz, and S. Roginski (Acta Physicochim. U.R.S.S., 1935, **3**, 503—508; cf. A., 1935, 942).—Results to be published (IV, V) are discussed. Comparison of rates of CO absorption and oxidation at 17° indicates that for $p_{CO_2} < 0.525$ mm. reaction takes place according to $CO+MnO_2=CO_2+MnO$. Above 0·525 mm. reaction is mainly CO (adsorbed)$+O_2$ (adsorbed) $\rightarrow CO_2$. The possibility of chain reactions is considered. O. D. S.

Speed of dissociation of carbon monoxide in presence of iron and its oxides. F. Meunier (Rev. Mét., 1936, **33**, 258—264).—The degree of dissociation of CO in the presence of Fe has been measured at temp. from 460° to 850°. At all temp. the rate of dissociation is very rapid at first but quickly falls. Thus at 525° the rate in the first sec. is about 12 times the rate after 75 sec. The results are discussed in relation to the reactions occurring in the different zones of the blast furnace. W. P. R.

Catalytic oxidation of carbon.—See B., 1936, 675.

Catalytic oxidation of carbon. H. M. Cassel (J. Amer. Chem. Soc., 1936, **58**, 1309—1310).—C, deposited on a glass surface from a gas flame, is more readily oxidised by O_2 at 600° when the glass surface is roughened than when it is smooth. The reaction is probably facilitated wherever two adjacent crystals touch each other or project into the gaseous phase. The catalytic effect of NaCl on the combustion of C is discussed in this light. E. S. H.

Catalytic properties of charcoal. I. "Peroxidase" activity. C. Schwob (J. Amer. Chem. Soc., 1936, **58**, 1115—1117).—The peroxidase activity of C in the indophenol reaction has been determined at room temp. and p_H 4·5. A hydrosol of C shows peroxidase activity in the formation of indophenol; no catalase activity has been observed. The C sol affects the e.m.f. of the cell $Pt|H_2O_2$, KCl $(0{\cdot}1N)|$ Hg_2Cl_2, Hg in the same way as does potato peroxidase. E. S. H.

Reduction of carbon dioxide to methane.—See B., 1936, 676.

Catalytic investigation of alloys. II. Decomposition of formic acid vapour on copper-silver alloys. G. Rienäcker and W. Dietz (Z. anorg. Chem., 1936, **228**, 65—76; cf. this vol., 941).—The decomp. of HCO_2H on Ag–Cu catalysts (3, 59, 84, 92, 97% Ag) was measured by a flow method at 180—235°. The activation energies for pure Cu and Ag were 21·6 and 18·8 kg.-cal., respectively. With 3% Ag (*i.e.*, with excess of Cu component embedded in eutectic) the val. was 17·3 kg.-cal. With 59% Ag it was 27·7 kg.-cal. The effect of composition on the activity of the catalyst is discussed. H. J. E.

Catalyst poisoning from the point of view of the specificity of active centres. I. Relative durations of sojourn of ethyl alcohol and acetaldehyde molecules on copper. II. Effect of temperature on relative durations of sojourn of ethyl alcohol and acetaldehyde, and true activation energy of ethyl alcohol dehydrogenation on copper. A. Bork and A. A. Balandin (Z. physikal. Chem., 1936, **B**, **33**, 54—72, 73—82).—I. The dehydrogenation of EtOH to MeCHO has been studied at 258° by a streaming method, and the effect of MeCHO examined. The rate is given by $dm/dt=k(M-m)/N$, where M and N are the no. of EtOH mols. and total no. of mols. of all kinds, respectively, passing over the catalyst in unit time and m is the no. of EtOH mols. decomposed in unit time, and k contains no adsorption magnitudes. The above durations of sojourn are equal, and $\gg$ that of H.

II. This equality persists down to 200°. The true energy of activation is 12,800 g.-cal. per mol., and even near equilibrium is uninfluenced by the back reaction. The logarithmic relation between the consts. of Arrhenius' equation holds (cf. this vol., 435). The heats of adsorption of EtOH and MeCHO on the catalyst are equal. R. C.

Vapour-phase catalytic oxidation of toluene.—See B., 1936, 682.

Mechanism of decomposition of methyl alcohol. E. Kuss (Angew. Chem., 1936, **49**, 483—486).—The decomp. of MeOH at surfaces of fused SiO_2, Ag wool, Pt gauze, Al, Cu, Fe, CaO, and compressed charcoal can be interpreted on the basis of the reactions (*a*) $MeOH \rightleftharpoons CH_2O+H_2$, (*b*) $2MeOH \rightleftharpoons Me_2O+H_2O$, (*c*) $Me_2O \rightleftharpoons CH_4+CH_2O$, (*d*) $Me_2O \rightleftharpoons CO+C+3H_2$, (*e*) $CH_2O \rightleftharpoons CO+H_2$, (*f*) $2CO \rightleftharpoons CO_2+C$. Ag and Al are the best sp. catalysts for reactions (*a*) and (*b*), respectively. Fe is initially a good catalyst for (*a*), but deteriorates rapidly owing to deposition of C produced by reactions (*e*) and (*f*). J. W. S.

Electrolytic oxidation of sodium chloride to sodium chlorate. L. Delavenna and J. Maillard (Compt. rend., 1936, **202**, 1663—1664).—The yield of $NaClO_3$ in the electrolytic oxidation of NaCl has been improved by preventing the escape of Cl_2 by rapid circulation of the electrolyte under pressure, employing a high anodic c.d., and cooling the liquid. With a c.d. at the anode of 20 amp. per sq. dm., in saturated NaCl at 0°, under a pressure of 400 cm. H_2O, the efficiency is 95% and $NaClO_3$ of 99·5% purity separates. M. S. B.

Electrolysis of aluminosilicates. M. S. Fortunatov (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, **2**, 257—259).—Electrolysis of molten 1 : 2 : 12 SiO_2–Al_2O_3–$NaHCO_3$ leads to deposition of Si at the cathode. Al is not deposited before most of the Si has been eliminated. R. T.

Electrolytic separation of polonium and radium-*D*. G. B. Pegram and J. R. Dunning (Physical Rev., 1935, [ii], **47**, 325).—Po and Ra-*D* can be completely separated from solutions and from each other by the use of the Fink–Rohrman rapidly-spinning disc cathode. L. S. T.

Effect of ultrasonic radiation on electro-deposits. W. T. Young and H. Kersten (J. Chem. Physics, 1936, **4**, 426—427).—Sound waves with a frequency of about 1700 kc. produce ripples in electro-deposited Fe, Co, Cd, Zn, brass, or black Ni. It is suggested that stationary waves are set up in the solution and that the metal ions are relatively more conc. in layers separated by half λλ. For Fe and Zn the best effect was obtained in conc. solutions. H. J. E.

Standardisation of photochemical methods for the measurement of solar ultra-violet radiation. H. S. Mayerson (Amer. J. Hyg., 1935, **22**, 106—136).—Methods of controlling errors in the bleaching of a $COMe_2$–methylene-blue mixture by light are given. The blackening of ZnS is satisfactory if the change in reflexion factor is measured. The $H_2C_2O_4$–UO_2SO_4 method is best. Ch. Abs. (*e*)

Reactions induced by the photoactivation of the water molecule. I. H. Fricke and E. J. Hart (J. Chem. Physics, 1936, **4**, 418—422).—Unbuffered gas-free solutions of MeOH in H_2O are decomposed to H_2 and CH_2O (about 10—20% of the H_2 formed) on irradiation with λλ 1850—2000 A. H_2O alone is unchanged, but it absorbs these λλ and serves to sensitise the decomp. of MeOH. H. J. E.

Catalytic decomposition of hydrogen peroxide in a bromine–bromide solution. Effect of light on the steady-state rate. R. Livingston and E. A. Schoeld (J. Amer. Chem. Soc., 1936, **58**, 1244—1246).—The rate is increased by light, but may be represented by $V=k[H_2O_2][H^{\cdot}][Br']$ for either the dark or light reaction. The increase in the abs. rate is explained by the increase in the steady-state [HBr]. The calc. average quantum yield for the reaction is < 1. E. S. H.

Influence of wave-length of light on the development of the latent image. (Mlle.) A. Tournaire and E. Vassy (Compt. rend., 1936, **202**, 1984—1986).—Measurements are recorded showing the effect of the time of development of the latent image on the density after development (for λλ 3520—2320 A.). The development of the latent image depends on the λ of the light used. H. J. E.

Photographic photometry in the extreme ultra-violet. (Mme.) R. Herman-Montagne, L. Herman, and R. Ricard (Compt. rend., 1936, **202**, 1668—1670).—When Na salicylate is used for sensitising Lumière plates (blue label) for use in the ultra-violet, the contrast factor for const. illumination is practically const. (to within 6%) not for the range 3000—1250 A. only, but also up to 700 A. These plates have been compared with those prepared by destroying the gelatin support of ordinary plates with dil. H_2SO_4. The latter are less sensitive than the former to strong but much more sensitive to feeble illumination, and are, therefore, more satisfactory for the detection of rays or bands of low intensity. M. S. B.

Photolysis of formaldehyde, acetaldehyde, and acetone at high temperatures. E. I. Akeroyd and R. G. W. Norrish (J.C.S., 1936, 890—894).—The results of previous workers are confirmed (cf. Leermakers, A., 1934, 976). MeCHO and CH_2O exhibit chain reactions; $COMe_2$ does not. From vals. of the temp. coeffs. obtained from velocity readings between room temp. and 400° heats of activation of 9·8 kg.-cal. for MeCHO and 16·0 kg.-cal. for CH_2O were obtained. A slight simplification of Leermakers' mechanism is proposed, and the propagation of the chains by Me radical carriers is confirmed. D. C. J.

Photochemical oxidation of formaldehyde and acetaldehyde. J. E. Carruthers and R. G. W. Norrish (J.C.S., 1936, 1036—1042).—The oxidation of CH_2O and MeCHO proceeds by short-length chains, that of CH_2O being through HCO_2H and of MeCHO through Ac_2O_2 (cf. A., 1930, 434). No peroxide or peracid is formed in the case of CH_2O. Quantum efficiencies for CH_2O+O_2 and $2CH_2O+O_2$ give vals. of 12·6 and 9·0 mols. per quantum absorbed, respectively. For the MeCHO oxidation, determined in a closed system and by a flowing method, vals. of the order of 20 mols. per quantum absorbed are obtained. D. C. J.

Mechanism of the photo-decomposition of acetone. R. Spence and W. Wild (Nature, 1936, **138**, 206; cf. this vol., 437).—At room temp. the photo-decomp. of $COMe_2$ yields 1·5 vols. of C_2H_6 to 1 of CO, and Ac_2 is also formed. At 60°, approx. equal amounts of CO and C_2H_6 are formed together with some CH_4. The primary photochemical process appears to be $COMe_2+h\nu\rightarrow Me+MeCO$ (cf. A., 1934, 1184). L. S. T.

Photochemical peroxide formation.—See this vol., 1091.

Photochemical decomposition of vitamin-*A*.—See this vol., 1159.

Photo-reduction of fluorescent substances by ferrous ions. J. Weiss (Nature, 1936, **138**, 80—81).—A reply to criticism (this vol., 907). L. S. T.

Effect of supersonic vibrations on chemical reactions. S. Sokolov (Tech. Phys. U.S.S.R., 1936, **3**, 176—182).—Exposure to supersonic vibrations tends to coagulate colloidal solutions which are on the point of coagulation, *i.e.*, those in which the size of the particles is relatively great. On the other hand in some cases in which the colloid is almost completely pptd. exposure to supersonic vibrations results in re-dispersion of the colloid. Numerous examples of both cases are cited. Supersonic vibrations produce inversion in slightly acid solutions of sucrose but not in neutral solutions. A. R. P.

Sonic activation in chemical systems: oxidations at audible frequencies. E. W. Flosdorf, L. A. Chambers, and W. M. Malisoff (J. Amer. Chem. Soc., 1936, **58**, 1069—1076).—A quant. investigation of the oxidation of H_2O, aq. NaCl, and aq. Na_2SO_3 at audible frequencies shows that the reactions are brought about by the production of activated O in association with cavitation. A compound of Na 3-aminophthalhydrazide and sonically-produced H_2O_2 can be energised to produce chemiluminescence in absence of the usual secondary oxidants. E. S. H.

Theoretical interpretation of radiochemical reactions via molecular clusters. R. LIVINGSTON (Bull. Soc. chim. Belg., 1936, **45**, 334—352; cf. A., 1934, 497).—A discussion of the various possible types of reaction occurring by α-ray activation, based on the theories of Lind and of Mund (A., 1931, 1139). A theoretical expression is developed for the ionic yield in the special case where the chemical reaction occurs inside the "clusters" which, when applied to the system Br_2–H_2–HBr, gives results in fair agreement with the experiments of Lind and Livingston (this vol., 688), and when applied to the polymerisation of C_2H_2 gives an expression very similar to that developed by Mund (A., 1931, 604). R. C. M.

Production of light water and determination of deuterium concentration in normal water. N. MORITA and T. TITANI (Bull. Chem. Soc. Japan, 1936, **11**, 403—413).—H_2 and O_2 obtained respectively by fractional and complete electrolysis of H_2O were combined to form light H_2O. In this way variations in *d* due to the electrolytic separation of O isotopes were eliminated. By comparing *d* with the val. for ordinary H_2O the ratio D : H in the latter is 1 : $\nless$5600. C. R. H.

Sodium xanthate. L. FILIPCZYK and M. KULESZA (Rocz. Chem., 1936, **16**, 245—253).—Pure Na xanthate (I) is prepared by adding excess of CS_2 to NaOEt in EtOH, and, after 30 min. at 0°, adding 5 vols. of Et_2O, collecting the ppt. of $NaCS_2(OEt),2H_2O$, and dehydrating in vac. at 35°. When (I) is dissolved in ordinary distilled H_2O an emulsion forms, and the titre of the solution (I in KI) falls rapidly, whilst with twice-distilled, CO_2-free H_2O the clear solution obtained remains unchanged for 3—10 hr. R. T.

Cuprous thiocyanate. Formation of coloured cuprous thiocyanate precipitates. D. KRÜGER, W. BÜSSEM, and E. TSCHIRCH (Ber., 1936, **69**, [*B*], 1601—1610).—Pure white CuCNS, obtained by slow, spontaneous decomp. of very dil. solutions of $Cu(CNS)_2$, has an *X*-ray diagram with very few lines and appears to have a cryst. form of high symmetry, probably hexagonal or trigonal. Black $Cu(CNS)_2$ gives a diagram with many lines and appears of lower symmetry. CuCNS obtained by addition of $Na_2S_2O_3$ to solutions of $Cu(CNS)_2$–H_2SO_4 appears rhombic and yields a diagram rich in lines; its formation cannot be attributed to $Na_2S_2O_3$ or $Na_2S_4O_6$ embedded in the lattice. Addition of small amounts of KI to neutral or acid solutions of $Cu(CNS)_2$ accelerates the separation of CuCNS and leads to the formation of ppts. ranging in colour from sandy to intensely violet. The possibility that the colour is due to adsorbed I is rendered improbable by the shade of the ppts. and excluded by the observation that violet deposits are obtained from solutions of $CuSO_4$–KCNS–KI of such small concn. that free I is not present. *X*-Ray examination of the violet material shows the presence of both modifications of CuCNS described above and a no. of new lines, including a very characteristic double line, not identical with those of CuI or $Cu(CNS)_2$ and ascribed to a third modification of CuCNS. H. W.

Order of affinity of metals for copper, iron, cobalt, and nickel. A. S. RUSSELL (Nature, 1936, **138**, 161).—Certain metals show a definite order with respect to their power of combining with Cu, Fe, Co, and Ni. For combination with Cu, the order is Al, Sn, Zn, Cd, Hg, and Pb. If Cu be competed for by two of these metals the one earlier in the series combines to the exclusion of the other. When added to a compound of Cu and one of these metals, a metal earlier in the series displaces the combined metal completely. Ternary and even quaternary compounds may temporarily be formed, but ultimately the metal lower in the series is set free. With a metal later in the series no reaction occurs. With Fe the most stable compounds are $AlFe_3$, $SnFe_2$, $ZnFe_7$, and $HgFe_4$ and the order is Al, Sn, Zn, Hg, Cd, and Pb. Neither Sn nor Zn can displace Al from $AlFe_3$, which is most easily prepared by adding Al to a Sn–Fe or Zn–Fe compound in Hg. With Co the most stable compounds are AlCo, $SnCo_2$, ZnCo, and HgCo, and with Ni, AlNi, Sn_4Ni_5, ZnNi, and HgNi. With Co and Ni, the order is the same as for Fe. L. S. T.

Cuprotartrates.—See this vol., 1093.

Complex compounds of dicarboxylic acid hydrazides. K. A. JENSEN and B. BAK (Z. anorg. Chem., 1936, **228**, 83—88).—The blue cryst. *compounds* $[Cu\{X(NH{\cdot}NH_2)\}_2]SO_4$ (X=CHO, Ac, or Bz) were prepared by interaction of aq. $CuSO_4$ with the corresponding hydrazide and pptn. with EtOH. Hydrazides of the dicarboxylic acids yielded a series of cryst. *compounds* of the general formula $[Cu\{(NH_2{\cdot}NH)C{:}O\}_2(CH_2)_n]SO_4$ (n=2—8). Hydrazides of $H_2C_2O_4$ and $CH_2(CO_2H)_2$ gave compounds of variable composition containing >1 atom of Cu to 1 mol. of hydrazide. H. J. E.

Reactions in the solid state. II. Investigation of the formation of copper ferrite by the Hahn emanation method. R. JAGITSCH and A. MASCHIN (Monatsh., 1936, **68**, 101—108; cf. A., 1935, 1333).—Addition of CuO to active Fe_2O_3 lowers the temp. at which the escape of emanation is a min. from approx. 950° to 850°. CuO has no effect up to 650°. Fe_2O_3 decreases the escape of emanation from active CuO at > 600°. Changes in activity with time at 660—800° were measured. The rate of formation of cryst. ferrite increases rapidly above 700°. H. J. E.

Dehydration of brucite. J. GARRIDO (Compt. rend., 1936, **203**, 94—95).—The dehydration of brucite at temp. between 500° and 1100° has been studied in relation to the crystal form of the MgO formed. C. R. H.

Mechanism of dehydration of calcium sulphate hemihydrate. H. B. WEISER, W. O. MILLIGAN, and W. C. EKHOLM (J. Amer. Chem. Soc., 1936, **58**, 1261—1265).—Isobaric dehydration gives a definite step, indicating that $CaSO_4,0{\cdot}5H_2O$ is a true hydrate. *X*-Ray examination shows that the hemihydrate and its dehydration product do not possess identical structures. E. S. H.

Preparation of anhydrous calcium sulphate. S. D. Wilson and L. Ting-Hsi (J. Chem. Eng. China, 1936, **3**, 131).—Anhyd. $CaSO_4$ for use as a laboratory desiccating agent is prepared from gypsum by heating at 160°, hydrating to give a slab of $CaSO_4,2H_2O$, breaking this up, screening, and heating the sized fragments separately at 240—260° for 2 hr. C. I.

Formation of crystalline calcium silicate hydrate. W. Köhler (Tonind.-Ztg., 1935, **59**, 739—740, 754—756; Chem. Zentr., 1935, ii, 3215).—Wollastonite was unchanged by heating for 14 days with 4 times its quantity of H_2O at 100°, 150°, 212°, and 290°. $2CaO,SiO_2$ when treated with H_2O at 212° and 290° formed $2{\cdot}2CaO,SiO_2,H_2O$, which commenced to lose H_2O at $>300°$. Hydrothermal treatment of $3CaO,SiO_2$ gave $Ca(OH)_2$ and doubly refractive needles of $CaO,SiO_2,0{\cdot}25H_2O$, which may also be prepared hydrothermally from a mixture of ground quartz and CaO. H. J. E.

Synthesis of hydrated monocalcium silicates under pressure. (Mlle.) J. Foret (Compt. rend., 1936, **203**, 80—83).—CaO and SiO_2, 1 : 1, heated under pressure in presence of H_2O at temp. between 100° and 200°, yield Ca_1 silicate of two different structures according as the temp. is $<$ or $>$ 140°. C. R. H.

Action of calcium carbide on methyl alcohol.—See this vol., 1091.

Crystallisation of zinc borate. R. Pâris and P. Mondain-Monval (Compt. rend., 1936, **202**, 2075—2077).—Crystallisation of $3ZnO,2B_2O_3$ commences at 500°. The rate increases to a max. at 820° and then decreases up to the m.p. (980°). H. J. E.

Argento-mercuric compound. P. Spacu (Compt. rend., 1936, **202**, 1987—1989).—The compound $Hg(CN)_2,AgNO_3,2H_2O$ has a characteristic *X*-ray spectrum, and is therefore not a mixture of $Hg(CN)_2$ and $AgNO_3$. H. J. E.

Antagonisms and alliances, experimentally demonstrated in effervescent and silent corrosion of aluminium, zinc, iron, tin, and lead in dilute acids, are of electrical nature. P. Ronceray (Bull. Soc. chim., 1936, [v], **3**, 1301—1303).—The electrical nature of corrosion is discussed. E. S. H.

Theory agrees with experimental results concerning intrinsic and extrinsic impurities in metals immersed in dilute acids. P. Ronceray (Bull. Soc. chim., 1936, [v], **3**, 1303—1306).—The rôle of impurities in the dissolution of metals in acids is discussed. E. S. H.

Alumina. T. Nakai and Y. Fukami (J. Soc. Chem. Ind. Japan, 1936, **39**, 203—204B).—Heating samples of $Al_2O_3,3H_2O$ obtained from different sources produced γ-Al_2O_3 at the same temp. but on subsequent further heating the change γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ took place at different temp. with the different samples. On heating $Al(NO_3)_3$, $Al(OAc)_3$, $Al_2(SO_4)_3$, and $AlCl_3$, γ-Al_2O_3 was first formed in all cases. T. W. P.

Preparation of synthetic zeolites. J. K. Delimarski (Bull. Sci. Univ. Kiev, 1935, **1**, 175—189).—Synthetic zeolite (I), in common with kaolin, undergoes exothermic transformation at 900—1000°. (I) is a salt of "permutic acid" (II), sols of which may be obtained by treating (I) with dil. HCl. Gels of (II) yield (I) when treated with 4—5*N*-NaOH; such gels as do not exhibit the exothermic transformation at 900° will not yield active (I). R. T.

[Reaction of tin with dilute acids.] P. Ronceray (Bull. Soc. chim., 1936, [v], **3**, 1290—1294).—Thin Sn foil, impure, but without external heterogeneity, dissolves in dil. HCl or H_2SO_4 with effervescence, but with thicker foil there is no effervescence. In the latter case, dissolution takes place through the reaction $Sn+2HCl+O \rightarrow SnCl_2+H_2O$. E. S. H.

By their antagonisms and alliances, corrosion reactions tend towards a maximum or a minimum. P. Ronceray (Bull. Soc. chim., 1936, [v], **3**, 1306—1309).—Observations on the corrosion of tinplate in dil. HCl are discussed. E. S. H.

Conditions for the preparation of oxide hydrates from ethylates and for the detection of hydrates from the *p–x* curves. P. A. Thiessen and R. Köppen (Z. anorg. Chem., 1936, **228**, 57—60; cf. A., 1931, 323).—A reply to criticisms by Weiser and Milligan (A., 1935, 433; this vol., 287). The formation of stable oxide hydrates of Sn, Si, Al, and Cr is reaffirmed. H. J. E.

[Reaction of lead with dilute acids.] P. Ronceray (Bull. Soc. chim., 1936, [v], **3**, 1294—1297).—Observations on the conditions under which effervescence occurs are reported. E. S. H.

Hexametaphosphoric acid. (Mme.) R. Salih (Bull. Soc. chim., 1936, [v], **3**, 1391—1396).—$H_6(PO_3)_6$ has been prepared by decomp. $Pb_3(PO_3)_6$ with H_2S. The aq. solution gives white gelatinous ppts. with $Ag^{\cdot}$ or $Pb^{\cdot\cdot}$. Conductometric titration curves with NaOH show that all the H atoms are replaceable, the first four more easily than the remaining two. E. S. H.

Preparation of hypophosphoric acid from PCl_3. J. H. Kolitowska (Rocz. Chem., 1936, **16**, 313—317).—PCl_3 is hydrolysed at 0° in an acetate buffer at p_H 5·7, and 0·1*N*-I is added; $H_4P_2O_6$ is obtained in 10% yield. The probable reaction is $O{:}PH(OH)_3+I_2 \rightarrow 2HI+[{\cdot}PO(OH_2)]_2$. R. T.

Isotopic separation of oxygen, chlorine, bromine, and nitrogen by chemical methods. E. Ogawa (Bull. Chem. Soc. Japan, 1936, **11**, 428—430).—Experiments which support the author's theories are described (cf. this vol., 1043). C. R. H.

Hydrolysis of sulphur by water below 100°. E. Cherbuliez and R. Weibel (Helv. Chim. Acta, 1936, **19**, 796—801).—Hydrolysis proceeds by the reaction $4S+3H_2O=2H_2S+H_2S_2O_3$. T. G. P.

Reactions of selenium oxychloride and selenium tetrachloride with pyridine.—See this vol., 998.

Polymetatelluric acid esters.—See this vol., 1097.

Hexaiodotellurates of aromatic amines and heterocyclic bases. T. Karantassis and L. Capatos (Compt. rend., 1936, **203**, 83—84).—The *hexaiodotellurates* of α- and β-$C_{10}H_7{\cdot}NH_2$, *m*-$C_6H_4(NH_2)_2$, benzidine, dianisidine, piperidine, and cinchonine have been prepared. The general formula is $I_6Te(HB)_2$ or I_6TeH_2B according to whether B (base) is uni- or bi-valent. They are cryst., anhyd., and hydrolysed by H_2O. C. R. H.

Preparation of Bjerrum's green hydrate of chromic chloride. M. G. de Celis (Anal. Fís. Quím., 1936, **34**, 553—556).—A modified method of prep. consists in slowly adding a solution of Recoura's chlorosulphate, cooled to 0°, to Et_2O saturated with HCl, at 0°, at the same time passing in a current of gaseous HCl. The yield of $[CrCl(H_2O)_5]Cl_2,H_2O$ is $>80\%$. L. A. O'N.

Extraction of uranium-*X* by ferric hydroxide precipitation. M. Bachelet (Compt. rend., 1936, **203**, 69—71).—Aq. $UO_2(NO_3)_2$ (200 g. per litre) is treated, in presence of Fe^{III} salt, with sufficient aq. NH_3 to give p_H 3·55, at which p_H little U is pptd. The $Fe(OH)_3$ ppt., containing U-X and some U, is collected, washed, and, after dissolving in HCl, is added to a solution of $(NH_4)_2CO_3$ and $(NH_4)_2S$. U-X and U dissolve as double carbonates and, after concn., HCl is added, and the solution boiled and filtered from S, which is inactive. Pptn. with aq. NH_3 followed by ignition of the ppt. yields U_3O_8 85—95% active. C. R. H.

Isotope exchange between hydrogen bromide and bromine. B. Topley and J. Weiss (J.C.S., 1936, 912).—Br containing the radioactive isotope is added to approx. equiv. amounts of dry HBr in CCl_4 solution, and the free Br immediately removed by Hg. The HgBr and the HBr in the filtrate are converted into AgCl and the sp. activities of the two AgBr samples are found to be equal. This complete interchange occurs at room temp. in <2 min. Possible mechanisms of the interchange are discussed. D. C. J.

Steel, partly tinned and polished, does not effervesce with dilute acids. P. Ronceray (Bull. Soc. chim., 1936, [v], **3**, 1297—1301). E. S. H.

Ferric hydroxides, and ferrous and silver ferrites. A. Krause (Rocz. Chem., 1936, **16**, 318—322).—Polemical, against Rodt (cf. A., 1934, 1320). R. T.

Preparation and composition of wustite phases. E. E. Wood and J. B. Ferguson (J. Washington Acad. Sci., 1936, **26**, 289—293).—Attempts to obtain FeO by heating $Fe(OH)_2$ prepared in an atm. of N_2 gave a product containing 80·4% FeO. The product always contained some Fe^{III}, the amount being the greater the higher was the temp. of dehydration. A wustite is probably a primary product. The action of heat on FeC_2O_4 in vac. does not give pure FeO. Fe and Fe_3O_4 produced by the thermal decomp. of wustite recombine at higher temp. An attempt to make FeO by the complete combination of Fe and Fe_3O_4 was unsuccessful. The limits of the wustite field were determined. A. J. M.

Metal carbonyls. Metal carbonyl hydrides. W. Hieber [with K. Krämer and H. Schulten] (Angew. Chem., 1936, **49**, 463—464; cf. A., 1932, 485; 1933, 685).—$Co(CO)_4$ (3 mols.) reacts with bases yielding *Co carbonyl hydride* $Co(CO)_4H$ (2 mols.) and $Co(CO)_3$ (1 mol.) with strong bases or $Co(OH)_2$ (1 mol.) with weak bases. The compound has m.p. −22° and decomposes above −18° yielding $Co(CO)_4$ and H_2. With complex *o*-phenanthroline–Ni and –Co ions it yields the *compounds* $[Co(CO)_4]_2[Ni(C_{12}H_8N_2)_3]$ and $[Co(CO)_4]_2[Co(C_{12}H_8N_2)_3]$. With conc. solutions containing $[Ni(NH_3)_6]^{\cdot\cdot}$ it yields the *compound* $[Co(CO)_4]_2[Ni(NH_3)_6]$. Action of conc. aq. NH_3 on $Co(CO)_4$ yields the *compound* $[Co(CO)_4]_2[Co(NH_3)_6]$. The series relationships of the Fe, Co, and Ni carbonyls and carbonyl hydrides and their structures are discussed. J. W. S.

Action of ammonium chloride on oxides. E. Montignie (Bull. Soc. chim., 1936, [v], **3**, 1388—1389).—Aq. NH_4Cl partly dissolves hydroxides of Mg, Sn, Cd, Zn, Mn, or Fe. With hydroxides of Ni, Co, Cu, and Hg the products are $NiCl_2,8NiO,13H_2O$ $CoCl_2,3CoO,3H_2O$, $CuCl_2,3CuO,xH_2O$, and $2HgCl_2,HgO$, respectively. Ag_2O is converted into AgCl. E. S. H.

Basic salts. XIV. Constitution of solid basic salts of bivalent metals. II. Basic nickel halides with simple laminated lattices. W. Feitknecht and A. Collet (Helv. Chim. Acta, 1936, **19**, 831—841; cf. this vol., 669).—The hydrolysis of aq. $NiCl_2$ above 100° yields $NiCl_2,3Ni(OH)_2$ or $NiCl_2,Ni(OH)_2$ according to the concn. An ill-defined basic bromide, of ideal formula $NiBr_2,3Ni(OH)_2$, has but a narrow homogeneity range. The lattices of these compounds have been studied by means of X-rays. T. G. P.

Recent advances in microanalysis. (Mlle.) A. Lacourt (Bull. Soc. chim. Belg., 1936, **45**, 189—212).—The trustworthiness of methods for determining the elements is tested (see also this vol., 1132). J. G. A. G.

Analytically useful efficiency of chemical reactions. A. Schleicher (Z. anal. Chem., 1936, **105**, 385—392).—The analytical efficiency of a reaction is made up of two factors, a capacity and an intensity factor; both factors can be derived from the abs. quantity in g. and the logarithm of the enrichment (a), where a is the product of the relation between the initial and final concn. of the reactants, and the relation of the reaction consts. A. R. P.

Foaming analysis. Wo. Ostwald and A. Siehr (Kolloid-Z., 1936, **76**, 33—46).—Foaming analysis is the production of a foam in a solution by agitation with a gas followed by continuous separation of the foam, thus giving a "spumate" and a residue. Apparatus and technique for foaming analysis are described. Examples of the recovery of dissolved substances from aq. solutions are given, and the technical applications of the process discussed. E. S. H.

Determination of acidity in heavy water mixtures. V. K. La Mer and S. Korman (Science, 1936, **83**, 624—626).—D substitution exerts an influence $>$ expected on the chemical properties of acid–base catalysis and acid dissociation consts. The quinhydrone electrode is satisfactory for measurements in the second case, and data are given for H_2O, quinol, AcOH, salicylic acid, etc. The effect of D substitution appears to be sp., but, in general, is more pronounced for weaker acids. The potential of the quinhydrone electrode in HCl and DCl solutions is 0·0345 volt more positive in D_2O than in H_2O, owing to unsymmetrical distribution of D in $QH_2+2DCl \rightleftharpoons QD_2+2HCl$. Other exchange equilibrium consts. are tabulated. L. S. T.

New fluorescent indicators (naphthionic acid and Schaeffer's salt). M. Déribéré (Ann. Chim. Analyt., 1936, [iii], 18, 173; cf. this vol., 810).—The fluorescence of Schaeffer's salt changes from zero below p_H 5·0, through bluish-violet and greenish-blue to bright blue above p_H 11. That of naphthionic acid changes from zero below p_H 3 to bright blue between p_H 6·5 and 9, thence to yellow-green between p_H 10 and 12. E. C. S.

Indicators. I. M. Kolthoff (Ind. Eng. Chem. [Anal.], 1936, 8, 237—239).—Future developments are discussed. E. S. H.

Preparation of diphenylamine indicator solution. H. M. State (Ind. Eng. Chem. [Anal.], 1936, 8, 259).—Dissolution in H_2SO_4 is facilitated by first melting the amine and then adding H_2SO_4 to the liquid. E. S. H.

Determination of chlorides.—See this vol., 1038.

Determination of active chlorine in bleach liquors.—See B., 1936, 692.

Vanadium sulphate as a reducing agent. II. Determination of chlorates, nitrates, and persulphates. P. C. Banerjee (J. Indian Chem. Soc., 1936, **13**, 301—304).—Chlorates and nitrates are reduced to chlorides and NH_3, respectively, by VSO_4, in boiling dil. H_2SO_4 and in a current of CO_2. The reduction of persulphates takes place at room temp. in the presence of Fe^{III} salt. In each case the excess of VSO_4 is titrated with $KMnO_4$ solution. C. R. H.

Application of Andrews' iodine monochloride method to the iodine bromide process. R. Lang (Z. anal. Chem., 1936, **106**, 12—23).—ICl solution treated with saturated aq. KBr in presence of CCl_4 first liberates I, which on further addition of KBr disappears again. This is attributed to the suppression of the [I′] through the action of excess of Br′, causing recombination of I and Br (produced by initial decomp. of IBr) re-forming IBr. Presence of KBr (1·3 mol. per litre) also prevents hydrolysis of IBr to yield HBr, I, and HIO_3, whereas KCl does not. To apply the IBr process to the determination of I or of I′ by KIO_3, the sample, containing $\not>$0·16 g. of I, is treated with 22 g. of KBr and 5 c.c. of conc. HCl and diluted to 100 c.c., 5 c.c. of CCl_4 being added. It is titrated with KIO_3 with vigorous agitation until the CCl_4 is decolorised. The method can also be used for titration of Sb^{III} etc. in presence of [HCl] too great for the ICl method. For titration of reducing agents, *e.g.*, CH_2O, 10 c.c. of 0·05*M*-CH_2O are treated with 5 c.c. of aq. ICl and 20 c.c. of 2·5*N*-NaOH in which 15 g. of KBr are dissolved. After 5—10 min., a further 22 g. of KBr are added and 10 c.c. of conc. HCl. The solution is diluted to 200 c.c. and titrated with KIO_3 in presence of CCl_4. Other oxidising agents [KIO_4, $KMnO_4$, $KBrO_3$, $KClO_3$, $Ce(SO_4)_2$, chloramine-*T*, Br, and $K_2Cr_2O_7$] can be used in place of KIO_3 in the titration of I′ by this method. J. W. S.

Nephelometric determination of fluorine [in minerals]. R. E. Stevens (Ind. Eng. Chem. [Anal.], 1936, 8, 248—252).—Decomp. of the mineral is effected by the Berzelius method and the resulting solution of F′ and NaCl is treated with gelatin, EtOH, and $CaCl_2$. CaF_2 is formed as a protected colloid and may be determined nephelometrically. The accuracy is about 1% of F. AsO_4''', SO_4'', and PO_4''' interfere and should be removed. E. S. H.

Fluorescence method for the determination of low concentrations of ozone. M. Konstantinova-Schlesinger (Acta. Physicochim. U.R.S.S., 1935, **3**, 435—450).—Small quantities of O_3 are determined by passing the gas through an alcoholic solution of dihydroacridine. The acridine formed by oxidation is determined by photometric measurement of the intensity of its fluorescence. O. D. S.

Volumetric determination of selenocyanate. G. Spacu and C. G. Macarovici (Z. anal. Chem., 1936, **105**, 408—410).—KCNSe can be titrated in 20% aq. KNO_3 (to prevent hydrolysis) with 0·1*N*-$AgNO_3$, using diphenylcarbazone as indicator. A. R. P.

Potentiometric titration of selenocyanate. R. Ripan-Tilici (Z. anal. Chem., 1936, **105**, 410—412).—The solution is titrated with $Hg(ClO_4)_2$ using an amalgamated Pt wire as indicator electrode. A. R. P.

Determination of arsenic in analytical reagents. C. Busquets (Anal. Fís. Quím., 1936, **34**, 557—579).—An apparatus for the rapid determination of small quantities ($\not<$0·0001 mg.) of As, by a modified Gutzeit method, is described. Limits of As permissible in the common reagents are tabulated. L. A. O'N.

Volumetric determination of antimony, arsenic, and iodide in the presence of bromide by L. W. Andrews' method. A. Mutschin (Z. anal. Chem., 1936, **106**, 1—11).—The acidity in the titration of Sb^{III} by Andrews' method (with KIO_3 in presence of CCl_4 or $CHCl_3$) is preferably 20 c.c. of conc. HCl (*d* 1·19) per 100 c.c. of final solution. It should be $\not<$15 c.c., but can be increased to 30 c.c. when large quantities of Sb are to be titrated; too high acidity retards the reaction. For the titration of $HSbO_2$ with KIO_3 in presence of ICl, the [HCl] should be 30—40 c.c. per 100 c.c. of final solution. Too little leads to hydrolysis of the ICl. Moderate addition of KBr or H_2SO_4, or dilution, does not affect the results. Potentiometric titration must be carried out in H_2SO_4 solution, the potential change for 0·025 c.c. of 0·025*M*-KIO_3 being 0·2—0·3 volt. The optimum [HCl] for the titration of As^{III} with KIO_3 in presence or absence of ICl is 30—40 c.c. per 100 c.c. of final solution. I′ can be titrated with KIO_3 by Andrews' method in presence of any quantities of Cl′ or Br′. J. W. S.

Micro-determination of silicon. F. De Eds and C. W. Eddy (J. Biol. Chem., 1936, **114**, 667—672).—Si is determined by addition of $(NH_4)_2MoO_4$ and reducing the resultant yellow complex to a blue one with *p*-hydroxyphenylglycine; the colour developed is compared with a standard in a photoelectric colorimeter. H. D.

Microchemical test for silicon. L. W. Staples (Amer. Min., 1936, 21, 379—383).—1 mg. of the mineral is heated with 2 mg. of fluorite and 2 drops of conc. H_2SO_4 in a Pt or Pb spoon at $\not> 75°$ for 10 min. The SiF_4 evolved is retained by 1 drop of dil. HNO_3 (1 : 7) placed on the underside of a celluloid slide covering the spoon, which is embedded in a charcoal block. A small particle of NaCl is added to the solution of H_2SiF_6 and the Na_2SiF_6 is identified under the microscope. Ge but not Zr, Ti, or Sn minerals give the test. BF_3 is not volatilised at the temp. used. The test is preferable to the metaphosphate bead, the Rb silicomolybdate, and the benzidine tests. L. S. T.

Determination of carbon monoxide in air.—See B., 1936, 693.

Aqueous alcoholic uranyl magnesium reagent. A. Krassilchik (Compt. rend., 1936, 203, 78—80).—Errors arising from the micro-determination of Na by means of Blanchetière's reagent are discussed and an improved technique is described. C. R. H.

Determination of silver by means of potassium ferricyanide. M. I. Perie and M. M. Lobunetz (Bull. Sci. Univ. Kiev, 1935, 1, 141—145).—Excess of standard $K_3Fe(CN)_6$ and 2—3 g. of KNO_3 are added to the solution at 80—90°, the solution is filtered (ppt. washed with 2% KNO_3), 1—2 g. of $ZnSO_4$ and 10 c.c. of 10% KI are added to the filtrate, and the I liberated is titrated with standard $Na_2S_2O_3$. The results are 0·3% low; if, instead of filtering, the ppt. of $Ag_3Fe(CN)_6$ is allowed to settle and a sample of the supernatant fluid is taken, the error is +0·6%. R. T.

Reaction adaptable to the volumetric determination of silver chloride. G. A. D. Haslewood (J.C.S., 1936, 1049).—Glacial AcOH added to a solution of AgCl in $Na_2S_2O_3$ gives a cryst. ppt. corresponding with $Na_5Ag_3(S_2O_3)_4,2H_2O$. The mother-liquor contains approx. 0·3 mg. per 100 c.c. calc. as AgCl. The ppt. from a known wt. of AgCl gives good results on dissolution in 0·01*N*-I and back titration with 0·005*N*-$Na_2S_2O_3$. D. C. J.

Rapid detection of silver halide in presence of silver cyanide. R. E. D. Clark (J.C.S., 1936, 1050).—On addition of HNO_3, $AgNO_3$, and 5% $HgNO_3$ solutions to a solution suspected of containing halide and CN′, the black coloration obtained if CN′ is present dissolves in excess of $HgNO_3$, leaving a permanent white ppt. if halides are present. D. C. J.

Gravimetric determination of barium by weighing as anhydrous oxalate. G. Díaz Villamil (Anal. Fís. Quím., 1936, 34, 580—586; cf. A., 1924, ii, 783).—Ba may be determined by pptn. as oxalate, drying in a current of air at 250° for 1 hr., and weighing as BaC_2O_4. This is definite and stable below 300°, and is little hygroscopic. It is not necessary to add EtOH before pptn. The accuracy is ±0·2%. L. A. O'N.

Determination of radioactivity. A. R. Olson, W. F. Libby, F. A. Long, and R. S. Halford (J. Amer. Chem. Soc., 1936, 58, 1313—1314).—Modified procedure is described. The radioactive material is dissolved and the solution introduced into a counter. E. S. H.

Sensitive reagents for the detection and determination of magnesium. F. P. Dwyer (J. Proc. Austral. Chem. Inst., 1936, 3, 184—186).—A 0·1% EtOH solution of *pp*′-dinitrodiazoaminobenzene when added to aq. $Mg(OH)_2$ gives a heliotrope colour, whilst *p*-nitrobenzenediazoamino-4-nitronaphthalene gives a sky-blue. $0·1 \times 10^{-6}$ g. of Mg per ml. may be detected with this reagent. *p*-Nitrobenzenediazoaminoazobenzene gives a cornflower-blue and 4-nitronaphthalene-4′-aminoazonaphthalene a cerise-blue. No hydroxide other than $Mg(OH)_2$ gives a colour with the latter. R. S.

Polarisation effects in the spectral analysis of zinc and tin. R. Breckpot (Natuurwetensch. Tijds., 1936, 18, 173—180).—Several elements (particularly In, Tl, Pb, Mg) show increased intensity when placed in the anode of an arc. Similar effects are observed, but to a smaller degree, with Sn. In these cases intensification is not due, as with Cu, to fractional volatilisation of the impurities. With Sn, As gives more intense lines in the cathode. Similar effects are obtained with either metals or oxides, and they are connected with the differences in ionisation potential of the impurities and the base metals. S. C.

Spectrographic investigation in analysis. J. van Calker (Z. anal. Chem., 1936, 105, 396—406).—The spectrum is excited by an arc of 30,000 volts at 0·02 amp. operated from a Röntgen inductor supplied with 15—20 amp. at 100 volts at the primary. The substance is placed in a small cavity in the lower electrode consisting of a Cu, Fe, or Ag wire 8 mm. thick. The technique adopted is illustrated by the qual. analysis of bauxite, by the detection of Pb in a Swedish bituminous coal shale, by the analysis of a mineral H_2O, and by the detection and determination of minute amounts of Hg. A. R. P.

Determination of cuprous oxide, cupric oxide, and copper in mixtures. Microscopical method. S. Zerfoss and M. L. Willard (Ind. Eng. Chem. [Anal.], 1936, 8, 303).—A statistical method is based on a microscopical count of the various particles, identified by the action of dil. HCl. E. S. H.

Potentiometric determination of cerous salts with ferrocyanide. I. A. Atanasiu (Z. anal. Chem., 1936, 105, 422—423).—Polemical against Spacu (this vol., 443). A. R. P.

Colorimetric determination of iron as $Fe(CNS)_3$. M. Bertiaux (Document. sci., 1935, 4, 49—52; Chem. Zentr., 1935, ii, 3135).—The effect of the concn. of the NH_4CNS solution on the intensity of the red colour has been studied. H. J. E.

Detection of ferricyanide ions in insoluble ferricyanides. L. Kuhlberg (Z. anal. Chem., 1936, 106, 30—32).—When HCl-sol. ferricyanides (*e.g.*, of Cd and Zn) or ferricyanides of metals with readily oxidisable hydroxides (Mn and Ce) are treated with a 1% solution of leuco-malachite-green in 50% HCl (I) and the solution diluted, a green colour is produced. $Hg_3[Fe(CN)_6]_2$ and $Cu_3[Fe(CN)_6]_2$ are detected by

decomp. with 1% $NiSO_4$ and addition of excess of NaOH, when the $Ni(OH)_3$ pptd. yields a green colour on addition of (I). $Ni_3[Fe(CN)_6]_2$ and $Co_3[Fe(CN)_6]_2$ can be treated directly with NaOH, the $Ni(OH)_3$ and $Co(OH)_3$ oxidising the reagent. $Fe(CN)_6'''$ in Turnbull's blue can be detected by treatment with 1% aq. Tl_2SO_4 and then with excess of NaOH. The ppt. [$Tl(OH)_3$, $Fe(OH)_3$ and $Fe(OH)_2$] is collected and treated with an AcOH solution of benzidine, when the appearance of a blue colour indicates presence of $Fe(CN)_6'''$. This method can also be used to detect the presence of $Fe(CN)_6'''$ in $Fe(CN)_6''''$.
J. W. S.

Potentiometric determination of tungsten. A. K. Babko (Bull. Sci. Univ. Kiev, 1935, 1, 147—153).—The W is reduced to W^V by Hg–Bi in conc. HCl, and the W^V is determined by electro-titration to W^{VI} by means of $K_2Cr_2O_7$. Reduction to W^{IV} involves the use of large amounts of Zn, and is not recommended. W^{III}, obtained as $[W_2Cl_9]'''$ by reduction with Hg–Pb at 50°, has a high potential, and its transition to W^V is not distinct. Hg–Pb in the cold gives W as a complex, $[WCl_5]''$, having a lower potential than $[W_2Cl_9]'''$, but considerable time is required for complete reduction. The method proposed consists in reduction with Hg–Pb to appearance of a red coloration (due to W^{III}), and oxidation to a potential of +0·1 volt (W^V), followed by further oxidation to W^{VI} (+0·35 volt).
R. T.

Separation of tungsten from tin by 8-hydroxyquinoline in presence of sodium oxalate. A. Jílek and A. Ryšánek (Coll. Czech. Chem. Comm., 1936, 8, 246—260; cf. A., 1933, 584).—The quantities of W found in W–Sn mixtures by the method previously given are high since the W ppt. retains some stannic acid. The wt. of ppt. obtained from 40—100 mg. of W and 5—200 mg. of Sn in a medium of aq. $Na_2C_2O_4$, NaOAc, 2% AcOH, and the reagent corresponds with the W, since the co-pptd. Sn compensates for the W left in solution. Double pptn. effects quant. separation. The solution is treated with 50 c.c. of 10% $H_2C_2O_4$, neutralised with NaOH, diluted to 200—250 c.c., and 2 c.c. of reagent (2 g. of 8-hydroxyquinoline in 5 c.c. of Ac_2O) are added to the solution at 60—80°. After 1 hr. the ppt. is removed, washed first with aq. $Na_2C_2O_4$ at 70°, then with reagent, and finally with H_2O, boiled with conc. H_2SO_4, cooled, and reheated after addition of H_2O_2. Excess of NaOH is added, and repptn. is effected with $H_2C_2O_4$ etc. as above. The ppt. is ignited in presence of $H_2C_2O_4$.
J. G. A. G.

Colour reactions of ter- and quadri-valent titanium. M. Schenk (Helv. Chim. Acta, 1936, 19, 625—639).—Aq. Ti^{III} and Ti^{IV} sulphates react to give a brownish-violet complex containing Ti^{III} and Ti^{IV} in the ratio 4 : 3. Ti^{III} sulphate gives an intense blue compound with conc. aq. alkali thiocyanates, but the reaction is unsuitable for quant. analysis. The reaction between Ti^{IV} solutions and H_2O_2 has been investigated.
T. G. P.

Separation of bismuth from lead and copper. E. A. Ostroumov (Z. anal. Chem., 1936, 106, 36—45).—Bi and Pb can be separated by Moser and Maxymovicz' Br'–BrO_3' hydrolysis method (A., 1926, 264), by Feigl and Ordell's pyrogallol method, or by Pinkus and Dernies' cupferron method (A., 1928, 1109). The method of Benkert and Smith (A., 1897, ii, 435) leads to irregular results. Bi can be separated from Cu by Moser and Maxymovicz' method and also by a modification of the cyanide method. In each case the first method is preferred. The pyrogallol method cannot be used in presence of a large excess of Cu.
J. W. S.

Specific reaction for bismuth by production of the monoxide. N. A. Tananaev (Z. anal. Chem., 1936, 105, 419—422).—The reagent, $K_4Mn(CN)_6$ (I), is prepared by adding aq. 10% $MnSO_4$ to a 0·5—0·33-saturated KCN solution until the ppt. first formed only just redissolves. On adding a Bi solution in 1 : 10 HCl to (I) a black ring of BiO forms at the interface. To detect Bi in Cu the metal is dissolved in HNO_3, $FeCl_3$ added followed by aq. NH_3, and the well-washed ppt. dissolved in 1 : 10 HCl for the test. Ag and Hg do not interfere.
A. R. P.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXXI. Determination of tungsten in earth-acid minerals. W. R. Schoeller and E. F. Waterhouse (Analyst, 1936, 61, 449—455; cf. this vol., 696).—The W is pptd. with the earth acids by tartaric hydrolysis at fairly high concn. (cf. A., 1934, 983) and then determined by pptn. with a slightly ammoniacal aq. Mg salt (A., 1935, 1217). High WO_3 contents lead to negative errors of 0·0003—0·002 g., and it is recommended that for such cases a correction, deduced by experiment on a synthetic mixture, be applied.
J. W. S.

Thermoregulator of the ordinary type, regulating the heating current without a relay. K. Kalinowski (Rocz. Chem., 1936, 16, 288—289).
R. T.

Apparatus for the maintenance of a graded series of constant temperatures. S. O. Mast (Science, 1936, 84, 69—70).
L. S. T.

Precision m.-p. apparatus. E. B. Hershberg (Ind. Eng. Chem. [Anal.], 1936, 8, 312—313).—A mechanically-stirred, electrically-heated, cyclic liquid bath for use with capillary-tube specimens is described.
E. S. H.

Micro-determination of b.p. of liquids at different pressures. E. E. Hays, F. W. Hart, and R. G. Gustavson (Ind. Eng. Chem. [Anal.], 1936, 8, 286).—The apparatus can be used for determining b.p. at pressures between 10 and 900 mm.
E. S. H.

Adiabatic calorimeter. W. Weinrich and H. Gaspari (Ind. Eng. Chem. [Anal.], 1936, 8, 307—310).—Apparatus in which the rate of O_2 absorption and rate of temp. change due to the heat of reaction of finely-divided substances with O_2 are measured is described. Adiabatic conditions are maintained by a differential thermopile and a photo-electric relay; the O_2 pressure is controlled automatically by an electronic relay and an electrolysis cell. Experiments with bituminous coal at 1 atm. and 50° initial temp. show that O_2 absorption and rise of temp. are nearly linear functions of time.
E. S. H.

Balanced circuit for resistance thermometers, combustible gas indicators, etc. M. G. Jacobson (Physical Rev., 1935, [ii], **47**, 336). L. S. T.

Simon desorption method between temperatures of 90° and 40° abs. A. van Itterbeek and W. Vereychen (Physica, 1936, **3**, 666—671).—Apparatus is described by means of which temp. of 67—45° abs. are obtained. O. D. S.

Spectral transmission of developed photographic emulsions. M. Roulleau (Compt. rend., 1936, **202**, 2066—2067).—Data for the transmission of various types of plate for λλ 8650—3650 A. are discussed. The type of developer used has a small influence. H. J. E.

Physical methods in chemical laboratories. XXXII. New method of quantitative emission spectrum analysis, applicable also as a micromethod. G. Scheibe and A. Rivas (Angew. Chem., 1936, **49**, 443—446).—The material is dissolved and about 0·01 c.c. of the solution placed on each electrode of a C arc. The initial spectrum is photographed over a period of 30 sec., the arc current being maintained const. The relative intensities of certain lines of each element are measured. The method is particularly applicable to the determination of traces of one metal in another and is illustrated by data for Mg in Al and Al and Cr in Fe. J. W. S.

Identification of crystalline materials. Classification and use of *X*-ray diffraction patterns. J. D. Hanawalt and H. W. Rinn (Ind. Eng. Chem. [Anal.], 1936, **8**, 244—247).—The identification of *X*-ray patterns by comparison with a collection of standard patterns is discussed. E. S. H.

Improved grating microspectrograph and its use in chemical microscopy. E. E. Jelley (J. Roy. Microscop. Soc., 1936, [iii], **56**, 101—112).—An improved grating instrument, allowing visual observation of orthoscopic and conoscopic interference effects and their spectra, is described. Spectra may be photographed without disturbing the adjustments of the crystal and polarising microscope. The dispersion is such that the distance between centres of adjacent perforations of the film corresponds with 50 mμ, the perforations providing an accurate λ scale. A Wollaston prism on a sliding mount provides for the study of pleochroism. A technique for studying and recording the dichroism and trichroism of minute crystals is described. N. M. B.

Arc support for routine spectroanalysis. R. Breckpot (Bull. Soc. chim. Belg., 1936, **45**, 375—378).—An improved form of Gramont's support is described. The electrode holders are detachable, thus permitting the removal of oxide dust which would otherwise cause contamination. Fumes should be drawn into a glass dust chamber above the arc. R. C. M.

Polarisation effects in the Hilger E1 quartz spectrograph. J. W. Ellis and J. Kaplan (Physical Rev., 1935, [ii], **47**, 255).—Serious limitations encountered when the light is partly or wholly polarised are described. L. S. T.

Technique of polarimetric determination in condensed gases. A. I. Schattenstein (Acta Physicochim. U.R.S.S., 1935, **3**, 53—60).—The method of determining the rotation of the plane of polarisation of optically active substances dissolved in condensed gases is described. The results of determinations of the sp. rotation of sucrose in liquid NH_3, and of santonamide in the presence of salts in liquid NH_3, are recorded. A. J. M.

Magneto-optic method of chemical analysis. III. Location of minima and quantitative analysis. S. S. Cooper and T. R. Ball (J. Chem. Educ., 1936, **13**, 326—328; cf. this vol., 949).—Procedure is detailed using salicylic acid as an example. L. S. T.

Photography of minima in magneto-optic apparatus. G. Hughes and R. Goslin (Physical Rev., 1935, [ii], **47**, 317).—The reality and reproducibility of the min. have been photographically demonstrated. L. S. T.

Automatic ionisation spectrometer. W. A. Wooster and A. J. P. Martin (Proc. Roy. Soc., 1936, A, **155**, 150—172).—An apparatus in which a crystal, having been once set, is moved automatically through a pre-arranged series of reflecting positions has been designed. The crystal and ionisation chamber are moved together slowly through the reflecting ranges while the ionisation current is automatically recorded, and rapidly in between. L. L. B.

Physical methods in chemical laboratories. XXXI. Determination of dielectric loss as a physico-chemical method of investigation. L. Rohde, P. Wulff, and H. Schwindt (Angew. Chem., 1936, **49**, 437—443).—The method of measurement of dielectric loss factor is described and its application to the testing of commercial oils etc. discussed. Presence of OH groups produces especially high losses. In presence of CO_2H groups, the loss factor increases with rising temp. to a max. and then decreases, this being attributed to the dissociation of double mols. J. W. S.

Mass spectrograph. W. B. Pietenpol (Physical Rev., 1935, [ii], **47**, 331—332).—A new type well suited to bracketing methods of determining isotopic wts. is described. L. S. T.

Construction and use of Geiger–Müller counters. G. L. Locher (Physical Rev., 1935, [ii], **47**, 326).—Technique of construction, criteria, and tests are described. L. S. T.

High-speed Geiger-counter circuit. H. V. Neher and W. W. Harper (Physical Rev., 1936, [ii], **49**, 940—943).—An improved circuit is described. N. M. B.

New ion source for mass spectroscopy. A. J. Dempster (Physical Rev., 1935, [ii], **47**, 331; cf. A., 1935, 677). L. S. T.

Measurement of small rapidly changing gas volumes. H. Lorenz (Z. Physik, 1936, **100**, 761—769).—Vols. of 0·1 c.c. changing within 0·1 sec. can be measured to 0·01 c.c. A. B. D. C.

Burette with automatic zero adjustment. J. Bitskei and B. Bitskei (Z. anal. Chem., 1936, **105**, 406—408).—The burette has a conical upper end which protrudes just inside a pear-shaped bulb having its lower end inclined downwards and joined to a thick-walled vertical tube passing to the bottom of the stock-bottle holding the standard solution. The bottle is provided with a side-tube and rubber bulb for forcing the liquid into the burette. A. R. P.

The micro-balance. G. GORBACH (Mikrochem., 1936, **20**, 254—336).—A comprehensive review.

Pressure regulator for a partial vacuum. E. CHERBULIEZ (Helv. Chim. Acta, 1936, **19**, 794—795). T. G. P.

Experimental methods for the kinetic study of the oxidation of metals. G. VALENSI (Bull. Soc. chim., 1936, [v], **3**, 1405—1422).—Apparatus and technique, with the corresponding methods of calculation of results, are described. E. S. H.

Jena glass apparatus for the chemical laboratory. P. H. PRAUSNITZ and H. SCHÄFER (Oesterr. Chem.-Ztg., 1936, **39**, 114—116).—New and modified apparatus is described. E. S. H.

Apparatus for determination of the adsorption of small quantities of gas by solutions. H. E. BENT, W. F. GRESHAM, and N. B. KEEVIL (J. Amer. Chem. Soc., 1936, **58**, 1307—1309).—Apparatus and procedure are described. E. S. H.

Electrodialyser. F. E. BARTELL (Ind. Eng. Chem. [Anal.], 1936, **8**, 247).—Apparatus is described. E. S. H.

Micro-vaporimetric determination of mol. wt. J. B. NIEDERL, O. R. TRAUTZ, and A. A. PLENTL (Ind. Eng. Chem. [Anal.], 1936, **8**, 252—255).—Modified apparatus for v.d. determinations of substances of b.p. $\not> 320°$ is described. E. S. H.

Measuring the thickness of thin, flowing, liquid films. H. H. BECK and K. G. WECKEL (Ind. Eng. Chem. [Anal.], 1936, **8**, 258—259).—The shift in the reflected beam, when an incident beam of light is directed on to the surface at 45°, gives a measure of changes in thickness of films covering the surface. E. S. H.

Making extremely thin films. J. D. HOWE and E. M. PURCELL (Physical Rev., 1935, [ii], **47**, 329; cf. this vol., 183). L. S. T.

Concentric cylinder viscosimeters. L. SQUIRES and R. L. DOCKENDORFF (Ind. Eng. Chem. [Anal.], 1936, **8**, 295—297).—By applying the relation between friction factor and Reynolds no., η of liquids can be determined in a concentric-cylinder viscosimeter even when the liquids are so fluid that their motion during the determination is turbulent. E. S. H.

Modification of the suspended-level viscosimeter. E. H. PAYNE and C. C. MILLER (Ind. Eng. Chem. [Anal.], 1936, **8**, 300—302). E. S. H.

Dynamic surface tension from liquid bells. E. BUCHWALD and H. KÖNIG (Ann. Physik, 1936, [v], **26**, 659—672).—In a method for the determination of the dynamic surface tension $\alpha_{\text{dyn.}}$ a stream of liquid impinges on a plate forming a liquid bell. A surface tension equation based on the theory of Boussinesq holds over a wide range of conditions if the thickness of the bell is > a certain val. $\alpha_{\text{dyn.}}$ is 5—8% > $\alpha_{\text{stat.}}$ for H_2O, EtOH, AcOH, and EtOAc, and 16·4% greater in the case of CCl_4, owing to diminished mol. orientation, whilst the $\alpha_{\text{dyn.}}$ and $\alpha_{\text{stat.}}$ of C_6H_6 are equal. R. S.

Preparation of flattened copper tubing coils. E. P. BARRETT and W. L. BARRETT (Ind. Eng. Chem. [Anal.], 1936, **8**, 311).—Procedure for flattening, coiling, and joining Cu tubes is described. E. S. H.

Laboratory stirrer. E. B. HERSHBERG (Ind. Eng. Chem. [Anal.], 1936, **8**, 313).—Agitation of solid–liquid mixtures is facilitated by attaching corrosion-resistant alloy wire to a glass stirrer. E. S. H.

Organic combustion apparatus for highly volatile and inflammable liquids. J. H. BRUUN and W. B. M. FAULCONER (Ind. Eng. Chem. [Anal.], 1936, **8**, 315—316). E. S. H.

Apparatus for [quantitative] semi-micro-hydrogenations. L. ZECHMEISTER and L. VON CHOLNOKY (Chem.-Ztg., 1936, **60**, 655—656).—A simple volumetric method, of accuracy 1—3%, for use at room temp. and in presence of a catalyst is described. R. C. M.

Illumination of menisci. J. ZELENY (Rev. Sci. Instr., 1936, [ii], **7**, 289; cf. Collins and Blaisdell, *ibid.*, 213).—A simple and efficient method, using white paper ruled at 45° with black lines, is described. N. M. B.

Technique for making sound ingots for density determinations. P. G. WALDO and W. P. DAVEY (Physical Rev., 1935, [ii], **47**, 338). L. S. T.

High-speed oil-diffusion pump. H. W. EDWARDS (Physical Rev., 1935, [ii], **47**, 259; cf. A., 1935, 840). L. S. T.

Centrifugal filtration tube. D. F. HOUSTON and C. P. SAYLOR (Ind. Eng. Chem. [Anal.], 1936, **8**, 302).—The centrifuge tube is provided with a filtration crucible, perforated support, and receiver for the filtrate. E. S. H.

Filter trains. P. BRUÈRE (J. Pharm. Chim., 1936, [viii], **24**, 49—58).—Filters for the ventilators of rooms used for collective gas protection are described and their control is discussed. F. N. W.

Ultrafiltration and concentration by ultrafiltration by a centrifuge method. R. BRINKMAN and J. VAN STEINFOORN (Biochem. J., 1936, **30**, 1523—1525).—By coating porcelain cylinders with water-glass, ultrafilters are obtained which are not clogged by the disperse phase, and will withstand prolonged use. 2 c.c. of filtrate can be obtained in 10 min. J. N. A.

Micro- and macro-Kjeldahl steam-distillation apparatus. J. M. FIFE (Ind. Eng. Chem. [Anal.], 1936, **8**, 316).—Modified apparatus is described. E. S. H.

Glass head for laboratory water still. P. F. SHARP and E. B. STRUBLE (Ind. Eng. Chem. [Anal.], 1936, **8**, 316). E. S. H.

Moisture tube. H. B. ALEXANDER (Ind. Eng. Chem. [Anal.], 1936, **8**, 314).—The apparatus is based on the principle of distillation with a H_2O-immiscible solvent. E. S. H.

Overhead heater for rapid evaporation, drying, and charring. L. F. Nims and M. K. Horwitt (Ind. Eng. Chem. [Anal.], 1936, **8**, 275).—Heating is by radiation from an electrical heating element, placed above the containers. E. S. H.

Battery-type stand assembly for distilling equipment. R. L. Mobley (Ind. Eng. Chem. [Anal.], 1936, **8**, 281). E. S. H.

Lecture experiment in combustion chemistry. K. Clusius and H. Gutschmidt (Angew. Chem., 1936, **49**, 446—447).—The temp. of an electric oven is raised slowly while a current of air is drawn through it and a drop of hydrocarbon periodically dropped in. The temp. when the drop first ignites spontaneously is noted. The temp. is then allowed to fall and the temp. noted when drops cease to ignite. Addition of 1% $Fe(CO)_5$ or 1·5% $EtNO_2$ raises or lowers the ignition temp., respectively, and illustrates the effects of knocks and antiknocks. J. W. S.

Distribution of gas in liquids. P. H. Prausnitz (Kolloid-Z., 1936, **76**, 227).—A lecture experiment, illustrating the influence of surface tension on bubble size, is described. E. S. H.

Conception of elements in chemistry. II. Ancient Greek philosophy. V. A. Plotnikov, I. L. Katznelson, and O. V. Bernschtein (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 3—36).—Philosophical. R. T.

Ruska's researches on the alchemy of Al-Razi. R. Winderlich (J. Chem. Educ., 1936, **13**, 313—315). L. S. T.

Béraut's theory of calcination (1747). D. McKie (Ann. Sci., 1936, **1**, 269—293).—Historical. E. S. H.

Precursors of rhenium and masurium. J. G. F. Druce (Chem. and Ind., 1936, 577—578).—Several of the unsubstantiated claims for the discovery of new elements during the last century possibly corresponded with Ma and two, perhaps, to Re, whilst others may have been Hf. R. C. M.

Geochemistry.

Content of heavy water (deuterium oxide) in medicinal mineral waters. K. Hansen, E. Rustung and J. Hveding (Klin. Woch., 1935, **14**, 684—685; Chem. Zentr., 1935, ii, 2921).—No deviation from the normal isotope ratio was detected in many medicinal waters. J. S. A.

Geochemical significance of the hydrolysis of sulphur by water. E. Cherbuliez and A. Herzenstein (Helv. Chim. Acta, 1936, **19**, 801—806; cf. this vol., 1079).—The origin of the S compounds and especially the significance of the ratio $H_2S : S_2O_3''$ in natural waters are discussed. T. G. P.

Alkali waters of the London chalk layers. J. Lepersonne (Bull. Soc. géol. Belg., 1934—1935, **58**, 38—63; Chem Zentr., 1935, ii, 3080).—Normal hard H_2O and strongly alkaline fresh H_2O are found. The latter comes from a base exchange in the glauconite-bearing sands, and contains $NaHCO_3$, Na_2SO_4, NaCl, NaBr, and NaI. H. J. E.

Mineral waters of Aréquipa, Peru. E. Pozzi-Escot (Bull. Soc. chim., 1936, [v], **3**, 1382).—Free Cl_2 and $NaIO_3$ have been detected. E. S. H.

Colorimetric determination of the p_H of some Peruvian waters. L. Pró y Castillo (Bol. Soc. Quim. Peru, 1936, **2**, 7—8).—The p_H vals. of natural waters (at the temp. of the source), and drinking waters have been determined. L. A. O'N.

Radioactivity of some natural springs in the Kabylie de Collo (Constantine, Algeria). M. Roubault (Compt. rend., 1936, **203**, 100—101).—Eight springs occurring in eocene schists and in granite masses were examined, those from the latter sources having the greatest activity. C. R. H.

Alkali metals in natural waters. R. Bossuet (Compt. rend., 1936, **203**, 63—65).—Natural waters of Corsica, Algeria, Tunis, and Madagascar are divided into two groups according to the presence or absence of Cs. C. R. H.

"Brown" snowfall in New Hampshire and Vermont. W. O. Robinson (Science, 1936, **83**, 596).—Dust of colloidal dimensions from the fall of brown snow at Wells River, Vermont, contained SiO_2 48·9, Al_2O_3 20·4, Fe_2O_3 6·1, CaO 5·4, MgO 3·2, loss on ignition 16·0%. L. S. T.

Sulphur in cyrtolite and its indication of galena. O. B. Muench (Amer. Min., 1936, **21**, 374—378).—The S determinations recorded throw no light on the low val. for the at. wt. of Pb obtained for Bedford cyrtolite (A., 1935, 558). Both samples of Bedford cyrtolite contained the same % S. L. S. T.

Mineralogy and origin of the Taconic limonites. D. H. Newland (Econ. Geol., 1936, **31**, 133—155).—Siderite is probably the parent source of much of the limonite of the Taconic belt of eastern New York and western New England. The deposits are consistently manganiferous (1—2%) and the high SiO_2 content (10—20%) is due partly to admixed detrital quartz and felspar and partly to amorphous SiO_2 in the groundmass. Appreciable amounts of carbonaceous matter are frequently present and pyrite and Zn are const. minor constituents. L. S. T.

Mineralised spherulitic limestone in the Cheltenham [St. Louis] fireclay. V. T. Allen (Amer. Min., 1936, **21**, 369—373).—The limestone described contains quartz, calcite, pyrite, ankerite, and sphalerite, probably deposited in this order. The spherulites have $CaCO_3$ 75·57, $MgCO_3$ 1·64, $Al_2O_3+Fe_2O_3$ 1·12, Na_2O, K_2O, and BaO none, insol. 18·88% [R. F. Rolufs]. The origin of the spherulites is discussed. L. S. T.

Nepheline contrasts. N. L. Bowen and R. B. Ellestad (Amer. Min., 1936, **21**, 363—368).—

Chemical analyses of nepheline from a Na-rich phonolite, typical of the E. African Rift, and from a K-rich melilite-leucite nephelinite, typical of the Central African Rift, show that the two nephelines are Na- and K-rich, respectively, emphasising, contrary to the view of Morozewicz (A., 1929, 45), the variability of the composition of nepheline and its control by the parent magma. L. S. T.

Metamorphic differentiation at contacts between serpentinite and siliceous country rocks. A. H. Phillips and H. H. Hess (Amer. Min., 1936, **21**, 333—362).—The changes in mineralogical composition, supported by chemical analyses, which have resulted from the permeation of hydrothermal solutions along contacts between serpentinite and siliceous country rock are described for several localities. An explanation of the origin of the mineral zones is given and the general process of metamorphic differentiation involved is discussed. L. S. T.

Ejected blocks of the Laacher See district. G. Kalb and P. M. Hopmann (Tsch. Min. Petr. Mitt., 1936, **48**, 1—26; cf. A., 1935, 60; 1936, 307).—Further examples are given of the formation of sanidinites of various kinds from cryst. schists. L. J. S.

Rare stylolites. P. B. Stockdale (Amer. J. Sci., 1936, [v], **32**, 129—133).—In all observed cases the origin is consistent with the solution theory.

Variation of the lead–uranium–thorium ratio in a single crystal of uraninite. C. M. Alter and E. M. Kipp (Amer. J. Sci., 1936, [v], **32**, 120—128; cf. this vol., 135).—Successive layers of a single crystal from Wilberforce, Ontario, were dissolved in HNO_3 and the following determinations made on the outer (I), intermediate (II), and central (III) sections. (I) was brown, and U had already been leached from it, but (II) and (III) were black and pure, and from these the age is now given as 760×10^7 years. (I) Pb 9·739, U 37·848, Th 8·360%; Pb/(U+0·36Th) 0·2383; (II) 11·927, 58·475, 14·093%; 0·1877; (III) 11·865, 60·699, 8·051%; 0·1866. L. J. S.

Tectonics of the Nemours region. M. Gautier (Compt. rend., 1936, **202**, 2092—2094). H. J. E.

Tin occurrence in marble at Arandis, S.W. Africa. P. Ramdohr (Neues Jahrb. Min., 1935, **A**, **70**, 1—48; Chem. Zentr., 1935, ii, 3080).—The minerals are described. H. J. E.

Thermal analysis of the hydrated iron ores of Krivoi Rog. V. A. Izbekov and K. J. Skartschenko (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, **2**, 31—44).—The presence and approx. content of hydrated ores can be determined from the heating curves of the ore, under standard conditions. R. T.

Zircon discoloured by sunlight (hyacinthine). K. Chudoba (Deut. Goldschmiede-Ztg., 1935, **38**, 303—304; Chem. Zentr., 1935, ii, 3219).—Zircons from Laacher Lake and Mongka lost their rose colour after 1 min. irradiation in direct sunlight and became grey. A brownish-red colour was restored by exposure to $RaBr_2$, or (more slowly) on keeping in the dark. The latter effect is due to radioactive substances in the mineral. H. J. E.

Rare earth content of European and Japanese argillite. E. Minami (Nachr. Ges. Wiss. Göttingen, 1935, IV, **1**, 155—170; Chem. Zentr., 1935, ii, 3218).—The average rare earth contents of European and Japanese palæozoic argillites were 0·0243 and 0·0225%, respectively. That of Japanese mesozoic argillite was 0·0173%. H. J. E.

Origin of the segmental coloration of amethyst and smoky quartz. C. Frondel (Amer. Museum Novi., 1935, No. 758, 15 pp.).—Examples are described. The phenomenon is attributed to the variation, with respect to crystallographic forms, of the rates of absorption of pigment during growth. Ch. Abs. (*e*)

Primary banding in basic plutonic rocks. R. R. Coats (J. Geol., 1936, **44**, 407—419).—The nature and suggested modes of origin of the mineralogically dissimilar bands often observed in basic plutonic rocks are reviewed. A mechanism, supported by experiments with labradorite and pyroxene, involving simultaneous crystallisation and differential settling of two or more minerals in a lighter magma, is suggested for the production of some of these bands. L. S. T.

Granitic sequence in the Southern Complex of Upper Michigan. R. M. Dickey (J. Geol., 1936, **44**, 317—340).—Granites representing three distinct periods of pre-Cambrian intrusion are described. L. S. T.

Helium content of beryls. H. J. Walke (Physical Rev., 1935, [ii], **47**, 969).—A discussion. The He content of beryls may be due to the disintegration of non-radioactive Be isotopes. L. S. T.

Sun-burning [of basaltic rocks]. W. Hoppe (Z. deut. geol. Ges., 1935, **87**, 452—473; Chem. Zentr., 1935, ii, 3220).—The phenomenon is found in basic but not in acid basalts. It differs from normal weathering in that it originates in the glassy material, in which hydrolysis and subsequent hydration occur. A grey layer is formed. It may be produced artificially by boiling for 40 hr. with H_2O, followed by prolonged treatment with CO_2. H. J. E.

Sun-burning [of basaltic rocks]. H. Stützel (Z. deut. geol. Ges., 1935, **87**, 473—480; Chem. Zentr., 1935, ii, 3220; cf. preceding abstract).—The characteristic appearance of the rock is described. H. J. E.

Immiscible silicate melts, approximating in their composition to that of natural rocks. D. P. Grigoriev (Zentr. Min., 1935, **A**, 242—254; Chem. Zentr., 1935, ii, 3219).—Melts of complex silicate tend to separate into two layers. A melt of alum (10), quartz (30), $MgCO_3$ (30), CaF_2 (5), and B_2O_3 (2 pts.) forms on slowly cooling an upper dark glassy layer containing tridymite, a lower layer of Mg mica, and an intermediate layer. H. J. E.

Baryte deposits of Virginia. R. E. Edmundson (Amer. Inst. Min. Met. Eng., 1936, Tech. Publ., 725, 17 pp.).—Baryte in Virginia occurs in fissure veins, replacement deposits, breccia zones, and residual deposits, in limestones and igneous rocks. The average content of BaO in the limestones is 0·06% and in a pegmatite 0·12%. The mineral could not have been derived by leaching from these country-rocks. It was no doubt deposited by magmatic waters. L. J. S.

Ore-body zoning. L. B. Riley (Econ. Geol., 1936, **31**, 170—184).—A method for examining ore-body zoning, *i.e.*, spacial variation of minerals and elements around and within an ore, is described. Examination of an incompletely oxidised Ag–Pb ore body at Sierra Mojada, Coahuila, Mexico, is used to illustrate the method, optical and microchemical tests being employed to detect the ions and minerals present. L. S. T.

Gold–bismuth occurrence in British Columbia. H. V. Warren (Econ. Geol., 1936, **31**, 205—211).—Galenobismutite (I) (Bi 51·00, Pb 30·50, Fe 1·50, S 16·40, total 99·40%) and cosalite (II) (Pb 41·20, Bi 39·35, Cu 3·60, S 16·40, total 100·55%) accompany the pyrite (III) which occurs massive or cryst. to the extent of 10—25% in the quartz veins of the Cariboo Gold Quartz Mine. Free Au is associated with (I) and (II), which proves the hypogene nature of the ore bodies. A telluride has also been found with (I). The paragenesis is probably (III) and quartz, followed by (III); galena and sphalerite; ankerite (?); (II), (I), and Au. L. S. T.

Minor intrusions of Glen Shee, Perthshire. W. O. Williamson (Geol. Mag., 1936, **73**, 145—157).—Additional data are given (cf. this vol., 185). L. S. T.

Xenolithic pegmatite in the Dalbeattie "granite." M. MacGregor (Geol. Mag., 1936, **73**, 171—185).—A pegmatite containing numerous xenoliths of more basic rock found in this "granite" is described. Interaction of the xenoliths and the pegmatite, and the origin of the xenolithic pegmatite, are discussed. L. S. T.

Heavy accessories of certain pre-Cambrian intrusives of the Canadian Shield. E. L. Bruce and W. Jewitt (Geol. Mag., 1936, **73**, 193—213).—All the granites from the different localities examined contain zircon, apatite, and titanite, and some contain rutile. The crystal habits of these heavy accessories vary widely. L. S. T.

Hierro and Gomera Islands (Canary Archipelago). E. Jérémine (Bull. Soc. franç. Min., 1935, **58**, 350—362).—Trachytes, basalts, limburgites, tephrites, and basaltic tuffs composing Hierro Island are described, and an analysis of ankaratrite from Ajate, near Valverde, is given. Trachytes, phonolites, trahitites, andesites, and basalts from Gomera are also described. L. S. T.

Tin deposits of Llallagua, Bolivia. E. Ahlfeld (Econ. Geol., 1936, **31**, 219—221).—A discussion of previous conclusions (A., 1935, 601). L. S. T.

Xenoliths in the Organ batholith, New Mexico. K. C. Dunham and M. A. Peacock (Amer. Min., 1936, **21**, 312—320).—The geology and mineralogy of large xenoliths near South Canyon and metamorphic effects are described. Green diopside [F. A. Gonyer] (SiO_2 53·10, TiO_2 0·17, Al_2O_3 2·55, Fe_2O_3 none, Cr_2O_3 none, FeO 0·97, MnO 0·08, MgO 17·25, CaO 25·80, H_2O 0·04, total 99·96%) is associated with the uvarovite. L. S. T.

Peculiar type of zoning in felspar. J. M. Trefethen (Amer. Min., 1936, **21**, 327—329). L. S. T.

Hydrothermal leaching in the Virginia mining district, New Mexico. S. G. Lasky (Econ. Geol., 1936, **31**, 156—169).—The tourmaline–Cu deposits of this district lie along veins that have been plugged and reopened repeatedly during the process of mineral deposition. Between the second and third stages of deposition the solutions removed calcite, sericite, and chlorite from interstitial and included fragments of altered wall rock in the veins, producing first- and second-stage minerals, chiefly specularite, quartz, and chalcopyrite, on which minerals of later stages were deposited. A mechanism is suggested to account for their presence at places previously traversed by alkaline or neutral solutions. L. S. T.

Hydrothermal experiments with lead and zinc minerals. O. H. Kristofferson (Econ. Geol., 1936, **31**, 185—204).—The extent to which $PbCl_2$ and $ZnCl_2$ can be transported in the vapour phase in presence of H_2O and HCl vapour at temp. $\ngtr$500° has been determined. Below 290°, sphalerites (ZnS) from various localities were unaffected by steam + 20% HCl. Above 290°, the Zn volatilises as $ZnCl_2$, and curves showing decomp. and volatilisation from 300° to 500° are given. Steam alone had no effect. Galena from Yellowstone, Wisconsin, is tarnished by steam above 300° owing to oxide formation. With steam and HCl in a dynamic system, volatilisation commences at 300°, and at 400° $PbCl_2$ accumulates in the system; at 475°, loss by volatilisation practically equals the amount of $PbCl_2$ formed, and above 475° the amount volatilised increases rapidly. The bearing of these results on the deposition of minerals is discussed. L. S. T.

Ice as an agent of rock weathering. O. R. Grawe (J. Geol., 1936, **44**, 173—182). L. S. T.

South Hill lamprophyre, Jersey. H. G. Smith (Geol. Mag., 1936, **73**, 87—91).—The mineral composition of the intrusion is described. L. S. T.

Reverse and oscillatory zoning in plagioclase felspars. E. S. Hills (Geol. Mag., 1936, **73**, 49—56).—A discussion of Phemister's theory (A., 1934, 862), and other possible causes of reverse zoning. L. S. T.

Pyroxmangite, new locality: identity of sobralite and pyroxmangite. E. P. Henderson and J. J. Glass (Amer. Min., 1936, **21**, 273—294).—Pyroxmangite (I) from Idaho has SiO_2 45·47 MnO 27·06, FeO 20·91, CaO 2·62, MgO 2·14, Fe_2O_3 1·50, H_2O 0·32, total 100·02% [E. P. Henderson] and α 1·737, β 1·740, γ 1·754 (±0·001). Physical, optical, chemical, and *X*-ray properties agree with those of the mineral from the original locality at Iva, S. Carolina. Sobralite from Sweden is identical with (I). Comparison of (I) and rhodonite shows differences in optical properties, and *X*-ray patterns indicate a structural difference which justifies the retention of both mineral species. L. S. T.

Amygdaloidal dykes. R. S. Moehlman (Amer. Min., 1936, **21**, 329—331). L. S. T.

Notation of polymorphic modifications. A. K. Boldyrev (Tsch. Min. Petr. Mitt., 1936, **47**, 517—

522)—Four different notations are noted; that which gives α, β, γ in the chronological order of discovery of each modification is recommended. For example, α-quartz (low quartz, quartz_{-575}, β-quartz of Boeke) and β-quartz (high quartz, quartz_{+575}, α-quartz of Boeke). Boeke's notation, according to the order of lower temp. stability, is not practicable when there are several modifications, as with ice and S. L. J. S.

Chemical composition of the titanomagnetites. G. Jouravsky (Compt. rend., 1936, **202**, 1689—1691).—The chemical composition and physical properties of titanomagnetites (I) are not in agreement with the assumption that they are solid solutions of magnetite and ilmenite in a state of false equilibrium through rapid cooling. Al_2O_3 and MgO are both present in considerable amount and may both play an important part in the formation of (I). M. S. B.

Uranotile. V. Billiet (Natuurwetensch. Tijds., 1936, **18**, 79).—*X*-Ray investigation confirms the formula $CaO,2UO_3,2SiO_2,6H_2O$. Uranotile forms rhombic crystals isomorphous with sklodowskite (A., 1924, ii, 868). D. R. D.

New cobalt minerals. L. de Leenheer (Natuurwetensch. Tijds., 1936, **18**, 77—78).—Three Co minerals found in Katanga (Belgian Congo) are described, viz., black ore, $2Mn_2O_3,3Co_2O_3,5CuO,15H_2O$ or $(Mn,Co)_2O_3,CuO,3H_2O$; boodtite, $5Co_2O_3,CuO,Fe_2O_3,11H_2O$ or $2[Co_2O_3(CuO,Fe_2O_3)],3H_2O$; and a mineral $3(Mn_2O_3,MnO_2),Co_2O_3,3CuO,8H_2O$. Mindigi spherocobaltite is a mixture containing 57% of rhombohedric mixed crystals of $CoCO_3$, $MgCO_3$, and $FeCO_3$, and small proportions of malachite, quartz, hæmatite, mindigite, chalcopyrite, bornite, linnæite, phyllite, cyanite, and tourmaline. D. R. D.

Dissolution, transportation, and precipitation of manganese. W. S. Savage (Econ. Geol., 1936, **31**, 278—297).—Primary Mn in rocks is dissolved mainly by the action of percolating carbonated waters. Peat solution is the next most effective solvent. Distilled H_2O is a poor solvent, but has a solvent action on the Mn in diabase $>$ that on the Mn in syenite. Oxygenated H_2O has the least solvent action, but is more effective on diabase than on syenite. Mn is transported chiefly as $Mn(HCO_3)_2$ in H_2CO_3-acid waters, and when these become neutral or slightly alkaline some unstable $Mn(OH)_2$ will be formed and remain in solution. Further transportation can take place with $Mn(HCO_3)_2$ and $Mn(OH)_2$ in unstable equilibrium until conditions which result in pptn. are encountered. The presence of org. matter in the H_2O does not appear to affect the transportation of Mn under these conditions. Conditions which effect pptn. such as aëration, the alkaline reaction of certain bacteria, and passage over a limestone bed are discussed. L. S. T.

Genesis of the Tri-state zinc and lead ores. J. Ridge (Econ. Geol., 1936, **31**, 298—313).—The jasperoid is composed of small xenomorphic crystals of quartz, the dark colour being due to org. matter. The paragenesis of the minerals is discussed. L. S. T.

Structure and primary mineralisation of the zinc mine at Balmat, New York. J. S. Brown (Econ. Geol., 1936, **31**, 233—258).—The geology of the district, the nature of the deposit and its constituent minerals are described. The origin of the Zn ores from solutions derived from underlying igneous masses, probably a pre-Cambrian granite, is discussed. A chemical and a mineralogical analysis of the ore are recorded. L. S. T.

Elasticity of rock melts. M. P. Volarovitsch and A. A. Leonteeva (Z. anorg. Chem., 1936, **228**, 28—32).—Measurements at 870—1120° on two basalts and one diabase are recorded. The temp. of initial crystallisation was 1060—1150°. H. J. E.

Economic application of the insoluble residue method. H. S. McQueen (Amer. Inst. Min. Met. Eng., 1936, Tech. Publ. 724, 12 pp.).—The residues obtained by treatment of limestone and dolomites or other sedimentary rocks containing $MgCO_3$ and $CaCO_3$ with dil. HCl permit correlations to be made between widely separated regions and different geological provinces. The successful economic application of the method in the drilling of H_2O, oil, and gas wells, in the study of ore deposits, and in the sp. investigation of limestones, is described. L. S. T.

Luminescence investigations with fluorites and other minerals. H. Haberlandt (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, **143**, 591—596; Chem. Zentr., 1935, ii, 3066; cf. A., 1935, 915).—The yellowish-white photo-fluorescence of certain fluorites is due to bituminous impurities. Lines of the rare earths and of U were observed for other specimens. H. J. E.

Synthetic emerald. Jaeger and Espig (Deut. Goldschmiede-Ztg., 1935, **38**, 347—349; Chem. Zentr., 1935, ii, 2992).—Synthetic emeralds identical in physical properties, crystal structure, zoned structure, etc. with the natural stone have been prepared and are now produced industrially. J. S. A.

Tin in Rumania. G. Cruglicov (Miniera, 1935, **10**, No. 5—6, 5—8; No. 7—8; 5—9; Chem. Zentr., 1935, ii, 2936).—Deposits in the mountains of southern Roumania are considered to be of economic val. J. S. A.

Formation of carbon dendrites. K. D. Luke, W. M. Madgin, and H. L. Riley (Nature, 1936, **138**, 161—162).—The formation of C dendrites by the cathodic reduction of colloidal solutions of graphitic oxide is described. L. S. T.

Crystals of pyrites in ironstone concretions in coal formations. A. Schoep (Natuurwetensch. Tijds., 1936, **18**, 167—172).—Ironstone (spherosiderite) consists of ankerite or some carbonate of similar composition and not of pure siderite. The reason for the occurrence therein of FeS_2 is discussed. D. R. D.

Alteration of coal seams by intrusion of igneous dykes.—See B., 1936, 674.

Rate of fall of meteoric material on the earth. C. C. Wylie (Physical Rev., 1935, [ii], 47, 192).—The annual amount of meteoric material estimated is 10 g. per sq. mile. L. S. T.

Organic Chemistry.

Variation of physical constants in homologous series. I. Hydrocarbons. V. G. Aranda (Anal. Fís. Quím., 1936, **34**, 513—524).—The mol. vol. at 20° of hydrocarbons is given by $V = aM+b$, where a is 1·155, the quotient of the increment for each CH_2 and its mol. wt. (M), and b is for paraffins 30·3; olefines 25·8; diolefines 21·3; *cyclo*pentanes 16·7; *cyclo*hexanes 14·8; *cyclo*heptanes 9·7; *cyclo*hexenes 6·4; *cyclo*hexadienes 4·4; aromatic hydrocarbons —0·8. Hence d_4^{20} is $1/(1{\cdot}155+b/M)$, where b has the above vals.; d is thus a hyperbolic function of M and when M is high, d for all the series approaches the val. 0·8658. n_D^{20} has similarly a common formula $(1{\cdot}815M+a)^{1/2}/(0{\cdot}825M+c)^{1/2}$, where, for the paraffins, a is 33·382, c 28·759; olefines, a 29·268, c 24·066; *cyclo*hexanes, a and c, 14·800; *cyclo*hexenes, a 6·786, c 6·207; aromatic hydrocarbons, a 0·358, c —1·379. n_D^{20} is thus a hyperbolic function of M tending to the val. 1·4832 for high vals. of M. The surface tension similarly may be represented $(2{\cdot}7857+d)^4/(1{\cdot}155M+b)$ and the parachor, $2{\cdot}7857M+d$, where b has the vals. given above and d is for paraffins 28·6; olefines 23·2; diolefines 17·8; *cyclo*hexanes 6·1; *cyclo*hexenes 0·7; *cyclo*hexadienes —4·7; aromatic hydrocarbons —10·1. F. R. G.

Decomposition of gaseous paraffins induced by ethylene oxide. L. S. Echols, jun., and R. N. Pease (J. Amer. Chem. Soc., 1936, **58**, 1317; cf. Heckert and Mack, A., 1929, 1243).—C_3H_8 and *n*- and *iso*-C_4H_{10}, but not C_2H_6, are "cracked" in presence of decomposing $(CH_2)_2O$ at 425°. The relative amount of olefine produced increases with the size of the paraffin and the amount initially present. Fletcher's results (this vol., 570) on the accelerated decomp. of MeCHO by $(CH_2)_2O$ are confirmed. H. B.

Action of nitrosyl chloride on *n*-hexane in presence of light. S. Mitchell and S. C. Carson (J.C.S., 1936, 1005—1006).—NOCl and *n*-C_6H_{14} in bright sunlight form a brown oil, which on steam-distillation gives $COMeBu^a$ and $COEtPr^a$. By excluding red light, a blue solution which probably contains ββ- and γγ-chloronitrosohexanes is obtained. The blue liquid undergoes two changes with red light; in the absence of O_2, oxime hydrochlorides are formed, and in its presence, photo-oxidation takes place. F. R. S.

Heptadecane. Action of selenium on stearic acid. S. H. Bertram (Chem. Weekblad, 1936, **33**, 457—459).—$C_{17}H_{36}$ is formed in approx. 50% yield by heating stearic acid with Se at 310—325°. The remainder is dehydrogenated to $C_{17}H_{34}$. There is no evidence of formation of oleic or elaidic acid. S. C.

Olefine formation. S. C. J. Olivier (Rec. trav. chim., 1936, **55**, 567—568).—Contrary to Taylor (A., 1935, 1465) $CHMeBr_2$ and KOH–aq. EtOH give mainly C_2H_3Br and a little C_2H_4, but no MeCHO. R. S. C.

Inhibition of chemical reactions. VI. Influence of ether and nitrobenzene on the absorption of ethylene by sulphuric acid.—See this vol., 1075.

Significance of organo-compounds of alkali metals in synthesis. K. Ziegler (Angew. Chem., 1936, **49**, 455—460, 499—502).—A review. E. W. W.

Effect of oxygen on reaction between bromine and butadiene. G. B. Heisig and H. M. Davis (J. Amer. Chem. Soc., 1936, **58**, 1095—1097).—Addition (method: A., 1935, 827) of Br (1 mol.) to butadiene (1 mol.) occurs much more rapidly with $\leqslant$2 mm. of O_2, the total pressure being atm. Reaction is fast even in presence of O_2 (2 and 375 mm.). These and previous results (*loc. cit.*) suggest a chain mechanism with short chains initiated at the surface. H. B.

Unimolecular elimination and the significance of the electrical conduction, racemisation, and halogen replacement of organic halides in solution. E. D. Hughes, C. K. Ingold, and A. D. Scott (Nature, 1936, **138**, 120—121).—$Bu^\gamma Cl$ absorbs Br quantitatively in SO_2 to yield *iso*butylene dibromide and HCl, suggesting a somewhat rapid equilibrium $Bu^\gamma Cl \rightleftharpoons CMe_2{:}CH_2+HCl$. Pure CHPhMeCl in pure SO_2 does not give a conducting solution, but addition of Br produces a quant. yield of $CHPhBr{\cdot}CH_2Br$. When conditions of purity are such that conduction takes place, $CHPh{:}CH_2$ and HCl are present. These results and others on racemisation, and unimol. replacement of halogen in SO_2, are grouped under a general mechanism in which ionisation of the halide determines the rate, and the instability of an alkyl cation containing a potential proton is responsible for the production of olefine. L. S. T.

Heavy chloroform, $CDCl_3$. R. Truchet (Compt. rend., 1936, **202**, 1997—1998).—Addition of D_2O to a suspension of CaO in $CCl_3{\cdot}CHO$ affords mainly *trichlorodeuteromethane*, b.p. 61·3—61·5°, as shown by its Raman spectrum which includes three pairs of lines, three polarisable and three non-polarisable. The increment in mol. refraction due to D is 1·11. J. L. D.

***s*-Tetrachlorodideuteroethane.** F. W. Breuer (J. Amer. Chem. Soc., 1936, **58**, 1289—1290).—C_2D_2 and Cl_2 in presence of light and a carrier (prepared by action of Cl_2 on a mixture of Fe_2O_3, Fe, Al_2O_3, Sb, and sand on asbestos) give *s*-tetrachlorodideuteroethane (I), b.p. 145·7±0·05°/737 mm. The v.p. of (I) at 20—80° is 6—9% < that of *s*-$C_2H_2Cl_4$. H. B.

Bromination of nitromethane.—See this vol., 1075.

Decomposition of methyl alcohol.—See this vol., 1076.

Synthesis under pressure of aliphatic compounds. (Sir) G. T. Morgan (Bull. Soc. chim. Belg., 1936, **45**, 287—312).—A review. At 400°/200 atm. using $CoSO_4$ with some CuO and MnO as catalyst, CO_2 and H_2 give a mixture containing MeOH (17%), EtOH (22%), higher alcohols, chiefly normal (11%), and CH_4 (47%). From EtOH and CO_2 at 370°/150 atm. Bu^aOH (19·5%), hexyl (4·6%), octyl (1·2%), and higher alcohols (1%) are obtained. Using H_3PO_4 and $Cu_3(PO_4)_2$ as catalyst at 330—340°, from MeOH, the largest yield of AcOH is 44·9% with 9·5% Me_2O. $EtCO_2H$ and higher acids may be obtained similarly in small yield from the corresponding alcohol, the active substance being the olefine derived by dehydration from the alcohol. F. R. S.

Action of calcium carbide on methyl alcohol. A. Contardi and B. Ciocca (R. Ist. lombardo Sci. Lett., Rend., [ii], 1935, **68**, 126—128; Chem. Zentr., 1935, ii, 3085).—$Ca(OMe)_2$ and C_2H_2 are formed vigorously at room temp.; hence CaC_2 cannot be used, in the presence of MeOH, for determination of H_2O. H. N. R.

Electrolysis of organic substances in non-aqueous media. II. G. Giacomello (Gazzetta, 1936, **66**, 350—357; cf. A., 1935, 1349).—Electrolysis of NaOMe in MeOH containing CO_2 yields at the cathode H_2, CH_4, CO_2, and some CO, and Na_2CO_3; that of NaOMe and HCO_2Me in MeOH gives H_2 and much more CO, with some CO_2 and CH_4. Conductivity of NaOMe–HCO_2Me mixtures suggests the formation of compounds, $HCO_2Me,NaOMe$ and $HCO_2Me,(NaOMe)_2$, probably enolic complex ions. Electrolysis of a mixture of NaOMe and $CO(OEt)_2$ yields H_2, CO_2, hydrocarbons, and CO, with resins at the anode. $ClCO_2Et$ also yields H_2 and CO_2. When NaOMe in MeOH containing CO_2 is electrolysed in a cell with porous compartments, both $Na^{\cdot}$ and CO_2 increase at the cathode. This is ascribed to the formation of $MeO{\cdot}CO_2Na$, dissociating into $[CO_2Na]^{\cdot}$ and OMe^-, the former yielding CO_2 and Na, and thus CO_2, H_2, and NaOMe. E. W. W.

Nitro-chromic reaction and its application to the determination of small quantities of alcohol. D. A. Webb (Sci. Proc. Roy. Dublin Soc., 1936, **21**, 281—284).—Modifications of Agulhon's reaction (cf. A., 1911, ii, 1140) described enable the [EtOH] to be determined to ±2%. The method is applied to small quantities of biological fluids. J. L. D.

Synthesis of monohydric unsaturated alcohols with systems of double linkings. P. Pelkis (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, **3**, 45—60).—$CMe_2{:}CH{\cdot}COMe$ (I), $CH_2{:}CH{\cdot}CH_2Br$, and Mg in Et_2O afford *βδ-dimethyl-$\Delta^{\beta\zeta}$-heptadien-δ-ol*, b.p. 58°/2 mm. (yield 75%). When $CHPh{:}CH{\cdot}COMe$ is taken in place of (I) the product is *α-phenyl-γ-methyl-$\Delta^{\alpha\epsilon}$-hexadien-γ-ol*, b.p. 122—123°/2 mm. (31% yield), whilst with $CHPh{:}CH{\cdot}COPh$ *αγ-diphenyl-$\Delta^{\alpha\epsilon}$-hexadien-γ-ol*, b.p. 170—170·5°/2 mm., is obtained, in 18·7% yield. R. T.

New constituents in the unsaponifiable matter of sperm blubber oil. S. Ueno and R. Koyama (Bull. Chem. Soc. Japan, 1936, **11**, 394—403).—Laborious fractionation of the unsaponifiable matter of the oil has yielded the following substances; heptanol (*4-iododiphenyl-4′-urethane*, m.p. 150°); octan-α-ol, b.p. 95—97°/17 mm. (further identified as its phenyl- and α-naphthyl-urethane); *alcohol* $C_9H_{20}O$, b.p. 102—105°/15 mm., oxidised to an acid (*amide*, $C_9H_{19}ON$, m.p. 97°); decan-α-ol (*phenylurethane*, m.p. 72·5°; *α-naphthylurethane*, m.p. 66°); dodecanol (*α-naphthylurethane*, m.p. 74°; two isomeric *phenylurethanes*, m.p. 71° and 69·5°, respectively), as a mixture of two isomerides named "*catadontidaeyl*" and "iso*catadontidaeyl alcohol*"; "*agorophyl alcohol*," $C_8H_{16}O$, b.p. 94—95°/15mm.; "*macrocephalyl alcohol*," $C_{10}H_{20}O$, b.p. 100—102°/15 mm.; alcohol, $C_{11}H_{22}O$, b.p. 140—141°/17 mm., converted by ozonolysis into *n*-nonoic acid and (probably) $H_2C_2O_4$, and therefore *Δ^{β}-undecen-α-ol*; "*odontocetyl alcohol*," $C_{12}H_{24}O$, b.p. 156—158°/17 mm.; ethers, $C_{18}H_{34}O$, b.p. 120°/17 mm. converted by hydrogenation (Pt-black) at 100 atm. into $C_{18}H_{38}O$, b.p. 223—224°/75 mm., and reduced by HI to decan-α-ol among other substances, thus indicating the constitution $C_{10}H_{21}{\cdot}O{\cdot}C_8H_{17}$. A. T.

Hydroxylation of the double linking. N. A. Milas and S. Sussman (J. Amer. Chem. Soc., 1936, **58**, 1302—1304).—$CHR{:}CHR'$ with $Bu^{\gamma}OH$–anhyd. H_2O_2 (prep. described) in presence of a little OsO_4 gives (mainly) $OH{\cdot}CHR{\cdot}CHR'{\cdot}OH$. The following are prepared: $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$; $OH{\cdot}CMe_2{\cdot}CHMe{\cdot}OH$; glycerol (from allyl alcohol); $OH{\cdot}CHPh{\cdot}CH(OH){\cdot}CO_2H$; $OH{\cdot}CHMe{\cdot}CH(OH){\cdot}CO_2H$; *dl*- and *meso*-tartaric acids (from fumaric and maleic acid, respectively). H. B.

Photochemical peroxide formation. III. Oxidation of glycerol by molecular oxygen in ultra-violet light. Photochemical production of perglycerol. R. Cantieni (Ber., 1936, **69**, [*B*], 1796—1798).—In analogy with the behaviour of primary alcohols, glycerol (I) is assumed to yield perglycerol (II), $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O_2H$ and the photo-oxidation of (I) to follow the course: $OH{\cdot}CH(CH_2{\cdot}OH)_2+7(II) \rightarrow 3H_2CO_3+H_2O+7OH{\cdot}CH(CH_2{\cdot}OH)_2$. The rate of formation of (II) diminishes when the concn. of (I) is $>10\%$. At the commencement of the reaction approx. equal amounts of (II) are produced in equal intervals of time, but the change tends towards an equilibrium. H. W.

Properties of the two modifications of glyceryl trinitrate. J. Hackel (Rocz. Chem., 1936, **16**, 213—222).—The formation of the stable modification of glyceryl trinitrate, m.p. 13°, is favoured by presence of $C_6H_3(NO_2)_3$ or kieselguhr, whilst cellulose nitrate and Et and Ph carbamate favour crystallisation of the unstable form, m.p. 1·9°; many other substances are without effect. The stable form is more sensitive to shock than the unstable one, but the explosive power and velocity of detonation are the same for both forms. R. T.

Explosions arising from ethers. E. C. Williams (Chem. and Ind., 1936, 580—581).—All ethers studied form peroxides on storage, but the rate of formation is variable. Danger occurs whenever an ether is dry-distilled, and with practically all ethers explosions have been experienced. Peroxides are determined by adding acidified KI–EtOH and titrating the I liberated; they may be destroyed by adding $FeSO_4$, $NaHSO_3$, acidified KI, or Na_2SO_3. The ether may also be distilled with steam. Oxidation inhibitors such as $NHPh_2$, α- and β-$C_{10}H_7{\cdot}OH$, and quinol retard development of peroxides. F. R. S.

Relative mobilities of normal alkyl radicals in their chlorothioformates. P. Carré and L. Peigné (Compt. rend., 1936, **202**, 2159—2161; cf. A., 1935, 1105).—The temp. of decomp. of $ClCOSR$ into RCl and COS in presence of quinoline ($R=n$-alkyl, C_1-C_{11}) shows an alternation effect with the no. of C in the radical. The results are compared with those of $ClCO_2R \rightarrow RCl+CO_2$ and discussed in terms of the mobility of the radicals. F. N. W.

Synthesis and hydrolysis of phosphoric esters derived by methylation of β-hydroxyethyl dihydrogen phosphate. O. Bailly and J. Gaumé (Bull. Soc. chim., 1936, 3, [v], 1396—1405).—Na_2 β-hydroxyethyl phosphate (I) with an equimol. amount of Me_2SO_4 gives Me β-hydroxyethyl H phosphate, isolated as *Ca* salt, which with dil. Na_2CO_3 at 100° is converted quantitatively into (I) (cf. A., 1926, 1225; 1935, 471). (I) with aq. $AgNO_3$ affords Ag_2 β-hydroxyethyl phosphate, which with $MeI–Ag_2O$ affords *Me_2 β-methoxyethyl phosphate*, b.p. 112—113°/9 mm., hydrolysed rapidly by cold *N*-NaOH to *Na Me β-methoxyethyl phosphate*, which when heated loses 50% of its P to give $NaPO_3$, but is stable in boiling *N*-NaOH (cf. A., 1926, 384). $OMe·[CH_2]_2·OH$ with P_2O_5 in anhyd. Et_2O affords β-methoxyethyl H_2 phosphate (*Ca, Sr*, and *Ba* salts). J. L. D.

Boric esters of polyalcohols. A. Dupire (Compt. rend., 1936, **202**, 2086—2087; cf. A., 1932, 937).—Almost quant. yields of the borates of $(CH_2·OH)_2$, glycerol, propane-αβ-diol, α-chloropropane-βγ-diol, and butane-αγ-diol were prepared from the alcohol and acid in presence of PhMe. H. J. E.

Boric acid derivatives of tetrasubstituted glycerol. P. Pastureau and (Mlle.) M. Veiler (Compt. rend., 1936, **202**, 1683—1685; cf. A., 1925, i, 500).—γ-Chloro-βδ-dimethylpentane-βδ-diol (cf. A., 1934, 753) with H_3BO_3 in H_2O gives a *H borate*, m.p. 132°. *H borates* (m.p. in parentheses) of the following are prepared: βδ-dimethylpentane-βγδ-triol (118°), βγδ-trimethylpentane-βδ-diol (72°), δ-chloro-γε-dimethylhexane-γε-diol (58°), and δ-chloro-ε-methyl-γ-ethylhexane-γε-diol (55°). Aryl-substituted glycerols do not give similar derivatives. J. L. D.

α-Halogenated thioethers. H. Böhme (Ber., 1936, **69**, [*B*], 1610—1615).—*CH_2Cl Et sulphide* (I), b.p. 128—131°/760 mm., is obtained in 60% yield by passing HCl into a suspension of polyoxymethylene in EtSH at room temp. It is hydrolysed by H_2O to CH_2O, EtSH, and HCl, which react with formation of $CH_2(SEt)_2$, b.p. 184°/763 mm. [also obtained from (I) and NaSEt in EtOH], and oxidised by H_2O_2 in AcOH to the sulphone, m.p. 104°. (I) and BzO_2H in $CHCl_3$ at −15° give *CH_2Cl Et sulphone*, b.p. 128°/14 mm., m.p. 33°. *$OEt·CH_2$ Et sulphide*, b.p. 134—136°/735 mm., is derived from (I) and NaOEt in EtOH or from $CH_2Cl·OEt$ and NaSEt. *$OEt·CH_2$ Et sulphone* has b.p. 122°/13 mm. *CH_2Ph Et sulphide*, b.p. 222—223°/750 mm., obtained from (I) and MgPhBr is oxidised to the *sulphoxide*, m.p. 49°, and sulphone, m.p. 84°. *Ethylthiolacetonitrile*, b.p. 72—73°/13 mm., from (I) and $Hg(CN)_2$, is hydrolysed by fuming HCl to ethylthiolacetic acid, b.p. 118°/11 mm. H. W.

Bromomethanetrisulphonates. H. J. Backer and P. Terpstra (Rec. trav. chim., 1936, **55**, 602—605).—Crystallographic and solubility data are given for the *Li_3* ($+9H_2O$), *Na_3* ($+3H_2O$), *Rb_3* (I) ($+H_2O$), *Cs_3* ($+H_2O$), *$Ba_{1\cdot5}$* ($+9H_2O$), and *tristrychnine* ($+3H_2O$) salts. *X*-Ray analysis of (I) is reported. R. S. C.

Structure of the isomeride of isoprenesulphone. H. J. Backer, J. Strating, and A. J. Zuithoff (Rec. trav. chim., 1936, **55**, 761—764).—$COEt·CH_2Cl$, b.p. 114° [obtained with $COMe·CHMeCl$ (I), b.p. 133—135°, from COMeEt and Cl_2], with $(NH_4)_2SO_3$ at 70° gives n-*butan-β-one-α-sulphonic acid* (*Ba* and *K* salt, hygroscopic). (I) gives similarly n-*butan-β-one-γ-sulphonic acid* [*Ba* ($+H_2O$) and *K* salts]. $OH·CH_2·SO_3K$ and $CH_2Ac·CO_2Et$ give a product, hydrolysed by H_2SO_4 to n-*butan-γ-one-α-sulphonic acid* (II) (*Ba* and *K* salts). Crystallographic data of the Ba salts are given. (II) is identical with the acid given by O_3, from the isomeride (ultra-violet illumination) of isoprenesulphone (A., 1935, 1105), the structure of which is thus proved to be 3-*methyl-4 : 5-dihydrothiophen* 1 : 1-*dioxide*. R. S. C.

Syntheses using tautomeric sodium organic compounds. G. V. Tschelincev (J. Gen. Chem. Russ., 1936, 6, 650—657).—Theoretical. R. T.

Reaction of iodoacetate and of iodoacetamide with thiol groups, with urease, and with yeast preparations.—See this vol., 1074.

Kinetics of hydrolysis of esters in alkaline media.—See this vol., 1073.

Action of liquid ammonia on acetone compounds of α-hydroxy-acids. H. Ôeda (Bull. Chem. Soc. Japan, 1936, **11**, 385—389).—*dl*-Lact-, *l*-leuc-, *dl*-mandel-, and *l*-α-hydroxy-β-phenylpropionamide were synthesised by treating the respective $:CMe_2$ compounds with liquid NH_3, best at −33°. A. T.

Keto–enol tautomerism of ethyl acetoacetate. M. Beyaert (Natuurwetensch. Tijds., 1936, **18**, 209—228).—The methods employed for determining the % of enol in keto–enol tautomerides in general and $CH_2Ac·CO_2Et$ in particular are reviewed. Equilibrium between the two forms of this ester is established only very slowly in the vapour phase, and attempts to determine the composition of the vapour at equilibrium were unsuccessful. The dielectric const. and *n* at various temp. of the pure keto-form and mixtures of this with the enolic form (up to 90% enolic) have been determined and follow the additive mixture law. D. R. D.

Condensation of acetaldehyde with ethyl α-methylacetoacetate. T. Wendling (Bull. Soc. chim., 1936, [v], **3**, 790—798).—$CHMeAc·CO_2Et$ (I), MeCHO (II), K_2CO_3, and H_2O at 5° give *Et α-methyl-α-(α′-hydroxyethyl)acetoacetate*, b.p. 87—88°/1·2 mm., which with AcCl gives the *acetate*, b.p. 108—111°/1·1 mm., and regenerates (I) and (II), slowly when kept and more rapidly at higher temp. It is decomposed by Ac_2O into (I) and (II), a trace of Et_2 ethylidenedi-α-methylacetoacetate being also formed. Attempts to prepare its pyrazolone failed, only that of (I) being isolated. H. G. M.

Preparation of hydroxy-acids [dihydroxystearic acid]. A. W. Ralston and S. T. Bauer (Oil and Soap, 1936, **13**, 170—171; cf. B., 1931, 199).

—A prep., m.p. 114—116°, consisting apparently essentially of the same dihydroxystearic acid, m.p. 124—127°, as is obtained by oxidising oleic acid (I) with alkaline $KMnO_4$, has been obtained by oxidising (I) in a solution containing NaOH (4%) and $Ni(NO_3)_2$ (0·5%) and a few crystals of $MnCl_2$ through which Cl_2 was bubbled. The intermediate formation of Ni_2O_7 is postulated. E. L.

Sodium xanthate.—See this vol., 1078.

Preparation of polyenes. Synthesis of hexatriene-αζ-dicarboxylic acid and octatetraene-αθ-dicarboxylic acid. R. KUHN and C. GRUNDMANN (Ber., 1936, **69**, [*B*], 1757—1765).—The synthesis follows the lines : $CHMe\dot{:}CH\cdot CO_2Et \rightarrow$
$CO_2Et\cdot CO\cdot CH_2\cdot CH\dot{:}CH\cdot CO_2Et \rightarrow$
$CO_2Et\cdot C(OAc)\dot{:}CH\cdot CH\dot{:}CH\cdot CO_2Et \rightarrow$
$CO_2Et\cdot CH(OAc)\cdot CH\dot{:}CH\cdot CH_2\cdot CO_2Et \rightarrow$
$CO_2H\cdot [CH\dot{:}CH]_2\cdot CO_2H$. Thus Et_2 α-acetoxymuconate is converted by Al–Hg in Et_2O–H_2O into *Et_2 α-acetoxy-αδ-dihydromuconate*, b.p. 144—146°/2 mm., hydrolysed by KOH–MeOH to Me_2 *trans-trans*-muconate, m.p. 56°, and by KOH–H_2O to *trans-trans*-muconic acid, m.p. 298° (Berl; decomp.). Similarly $CMe_2\dot{:}CH\cdot CO_2Me$, KOEt, and $Et_2C_2O_4$ afford the *K* salt, $CO_2Et\cdot C(OK)\dot{:}CH\cdot CMe\dot{:}CH\cdot CO_2Me$, converted by successive treatment with Ac_2O, Al–Hg, and hydrolysis into trans-trans-β-*methylmuconic acid*, m.p. 232° (decomp.). Et_2 α-acetoxy-$\Delta^{\alpha\gamma\epsilon}$-hexatriene-αζ-dicarboxylate is converted into *Et_2 α-acetoxy-$\Delta^{\beta\delta}$-hexadiene-αζ-dicarboxylate* (I), b.p. 158—160°/1 mm., hydrolysed by KOH–MeOH–H_2O to *$\Delta^{\alpha\gamma\epsilon}$-hexatriene-αζ-dicarboxylic acid* (II), m.p. 316—318° (decomp.) when placed in bath at 250° and quickly heated, gradual decomp. > 280° when slowly heated [*Me_2* ester, m.p. 172°, from (II) through the acid *chloride* or with CH_2N_2, but best obtained from (I) and KOH–MeOH; *Et_2* ester, m.p. 90°]. (II) and Br in diffuse daylight afford αβγδεζ-*hexabromosuberic acid*, gradual decomp. > 200°. (III) is hydrogenated (PtO_2 in 0·1*N*-NaOH) to suberic acid, m.p. 141—142°. (II) is reduced by Na–Hg to *$\Delta^{\beta\delta}$-hexadiene-αζ-dicarboxylic acid*, m.p. 190°, the constitution of which is established by its condensation with $CHPh\dot{:}CH\cdot CHO$ in presence of Pb oxide and Ac_2O to αμ-diphenyl-$\Delta^{\alpha\gamma\epsilon\eta\iota\lambda}$-dodecahexaene, m.p. 262°; it is isomerised by boiling 20% KOH to *$\Delta^{\alpha\gamma}$-hexadiene-αζ-dicarboxylic acid*, m.p. 225—227°. Et γ-methylsorbate, $Et_2C_2O_4$, and KOEt afford *Et ethoxalyl-γ-methylsorbate*, m.p. 103·5°, transformed by successive treatment with Ac_2O, Al–Hg, and KOH–H_2O into *γ-methyl-$\Delta^{\alpha\gamma\epsilon}$-hexatriene-αζ-dicarboxylic acid*, m.p. 296° (decomp.). $Et_2C_2O_4$ and Me octatrienecarboxylate in presence of KOEt give *Et ethoxalyloctatrienecarboxylate*, m.p. 119—120°; condensation occurs better in presence of $KOPr^{\beta}$. The mixture of esters is converted by Ac_2O followed by Al–Hg and KOH–MeOH into *Me_2 $\Delta^{\alpha\gamma\epsilon\eta}$-octatetraene-αθ-dicarboxylate*, m.p. 212°, hydrolysed by 5% KOH to *$\Delta^{\alpha\gamma\epsilon\eta}$-octatetraene-αθ-dicarboxylic acid*, m.p. 309°/(decomp.), which is reduced by Na–Hg to *$\Delta^{\beta\delta\zeta}$-octatriene-αθ-dicarboxylic acid*, m.p. 195° (decomp.). H. W.

Acyclic keto-acids. N. A. PREOBRASHENSKI, M. N. SCHTSCHUKINA, and A. F. VOMPE (Ber., 1936, **69**, [*B*], 1618—1620).—Et_2 ethylsuccinate, $Et_2C_2O_4$, and NaOEt in Et_2O at room temp. yield *Et_2 ethoxalylethylsuccinate* (yield 80—90%), which passes when distilled under diminished pressure into CO and Et_3 butanetricarboxylate. It is hydrolysed by boiling conc. HCl to *γ-keto-α-ethylglutaric acid* [*semicarbazone*, m.p. 177—178° (decomp.); 1-*phenyl-5-ethylpyridazin*-6-*one*, m.p. 159—160° (decomp.)], the *Et* ester, b.p. 148·5°/15 mm., 269°/741·5 mm. (*semicarbazone*, m.p. 130·5—131°), of which condenses with HCO_2Et to *Et_2 γ-keto-β-aldehydo-α-ethylglutarate*; this could not be distilled without decomp. and gives a phenylhydrazone and semicarbazone which are difficult to purify. H. W.

Rotatory power of methyl tartrate : influence of solvent, temperature, and neutral salts. Y. K. HENG (Bull. Soc. chim., 1936, [v], **3**, 1004—1019).—In aq. solution α is reduced by the addition of neutral salts. The effect depends on the cation, showing a periodicity which corresponds with the periodic table. Salts of Fe^{III} and Th increase α. The influence of temp. varies according to the solvent. E. S. H.

Cuprotartrates. Y. K. HENG (Bull. Soc. chim., 1936, [v], **3**, 993—1004).—The reactions of NaOH + $Cu(OH)_2$ with tartramic acid, tartramide, and Me tartrate have been investigated by following the change in optical rotation. The curves obtained show the existence of the *salts* $2C_4H_4O_5NH_2,CuO$, $[CuO,C_4H_4O_5NH_2]Na_2$, $[2C_4H_4O_4(NH_2)_2,CuO]Na_2$, and $[C_4H_4O_4Me_2,CuO]Na$. E. S. H.

Preparation and constitution of alginic acid. V. C. BARRY and T. DILLON (Sci. Proc. Roy. Dublin Soc., 1936, **21**, 285—287; cf. A., 1932, 931; 1935, 550).—Extraction of the fronds of *Laminaria digitata* with aq. NH_3 (details given) affords alginic acid, $C_6H_{10}O_7$ (equiv. wt. 192; $[\alpha]_D^{10}$ −133·4° in H_2O, for the Na salt, which supports the view that the polymerising unit is the uronic acid). J. L. D.

Derivatives of alginic acid. I. Acetylation of alginic acid. V. C. BARRY, T. DILLON, and P. O'MUINEACHÁIN (Sci. Proc. Roy. Dublin Soc., 1936, **21**, 289—296).—Alginic acid (I) (cf. preceding abstract) affords a trace of Ac_1 (?) with NaOAc and boiling Ac_2O and a *Ac_3* derivative with Ac_2O containing $ZnCl_2$ at 80°. (I) with boiling Ac_2O containing a little I affords *Ac_3* and *Ac_2* derivatives and with HI in Ac_2O affords, in good yield, *Ac_2* derivatives, $[\alpha]_D^{8}$ −93·1°, −113·9°, and −136·8° (Na salt) in H_2O, respectively, which are probably derivatives of degradation products of (I) of different degrees of polymerisation. The results support the view that the entire uronic acid is the polymerising unit. J. L. D.

Glycuronic acid. A. LEULIER (J. Pharm. Chim., 1936, [viii], **24**, 64—76, 122—131).—A review.

***n*-Butyl esters of thio-acids.** E. MÜLLER and A. FREYTAG (J. pr. Chem., 1936, [ii], **145**, 318—320).—$NaBu^{a}SO_4$ (modified prep.), aq. KOH, and CS_2 give $Bu^{a}SH$, which with $Pb(OAc)_2$–EtOH affords the stable *Pb* salt. With the appropriate acid chloride in Et_2O this gives >80% yields of S-*Bu^{a} thiopropionate*, b.p. 64·5°/15 mm., *-butyrate*, b.p. 80·1°/12 mm., and -iso*valerate*, b.p. 86·5°/12 mm., only slowly attacked by oxidising agents. R. S. C.

αβ-, αγ-, βγ-Disulphobutyric acids. H. J. Backer and N. Benninga (Rec. trav. chim., 1936, **55**, 605—614).—$SO_3H\cdot CHMe\cdot CH_2\cdot CO_2H$ and oleum at 90° give mainly αβ-*disulphocrotonic acid*, hydrogenated (Pt-black) in dil. AcOH to αβ-*disulphobutyric acid* ($Ba_{1\cdot5}$, $+2H_2O$, and Tl_3 salts), the *tristrychnine* salt, $+9H_2O$, of which, when recrystallised, yields the d-*acid* (I), $[M]_D$ +16° in H_2O (Na_3 salt, $[M]_D$ −6° in H_2O). The non-resolvable acid (A., 1935, 1107) is thus proved to be the ββ-disulpho-acid. $Br\cdot[CH_2]_3\cdot CO_2NH_4$ and $(NH_4)_2SO_3$ at 135° give γ-*sulphobutyric acid*, $+0\cdot5H_2O$, m.p. 93—93·5° [*distrychnine*, $+2\cdot5H_2O$ (non-resolvable), *Ba*, $+5H_2O$, and Ag_2 salts; Me_2 ester, b.p. 150—153°], which with oleum at 85—95° gives αγ-*disulphobutyric acid* ($Ba_{1\cdot5}$ salt, $+8H_2O$), the *tristrychnine* salt, $+8H_2O$, of which leads to the active *acid* (II), $[M]_D$ 7·2° ($Ba_{1\cdot5}$ salt, $[M]_D$ +9·1°). $CH_2Cl\cdot CH{:}CH\cdot CO_2NH_4$ and $(NH_4)_2SO_3$ at 50° give γ-*sulphocrotonic acid* (III) ($+0\cdot5H_2O$), m.p. 94—96° after sintering at about 87°, hygroscopic (*Ba*, $+3H_2O$, Na_2, hygroscopic, Ag_2, and *diquinine*, $+1\cdot5H_2O$, salts; *dichloride*, b.p. 118—121°/2 mm.; Me_2 ester, b.p. 140—142°/2 mm.; *monoamide*, hygroscopic solid), which with $(NH_4)_2SO_3$ at 80° gives βγ-*disulphobutyric acid*, $+2H_2O$, m.p. 95°, hygroscopic [$Ba_{1\cdot5}$, $+H_2O$, and Tl_3 salts; also obtained from $CHCl{:}CH\cdot CH_2\cdot CO_2NH_4$ and $(NH_4)_2SO_3$ at 65°], the *tristrychnine* salt, $+5H_2O$, decomp. about 245°, of which leads to the d-*acid* (IV), $[M]_{5460}$ +59° in H_2O ($Ba_{1\cdot5}$ salt, $[M]_{5460}$ +59° in H_2O). (I) and (II), having an α-SO_3H, racemise in hot alkali, but (IV) does not. The addition of $KHSO_3$ to (III) at 80° in 0·1*M* and 0·5*M* solution has *k* 0·64 and 1·24, respectively, compared with 187 for $CHMe{:}CH\cdot CO_2H$ in 0·1*M* and 0·063 for $SO_3H\cdot CMe{:}CH\cdot CO_2H$ in *M* solution. R. S. C.

Formation of carbonyl compounds by the explosive decomposition of nitric esters. G. Denigès (Compt. rend., 1936, **202**, 1998—2000).—Me, Et, Pr^a, Pr^β, Bu^a, Bu^β, CH_2Ph, and α-phenylethyl nitrate decompose when heated to give CH_2O, MeCHO, EtCHO, $COMe_2$, PrCHO, COMeEt, PhCHO. and COPhMe, respectively. The rate of reaction is much decreased in CO_2. Aldehydes corresponding with the higher esters undergo secondary decomp. J. L. D.

Isomerisation of hydroxyaldehydes. VI. S. N. Danilov and A. M. Gachokidze (J. Gen. Chem. Russ., 1936, **6**, 704—719).—β-Bromoglucose tetra-acetate in 50% AcOH and Zn at 15—25° yield glucal triacetate, the Br_2-, Br_1-, Cl_2-, or Cl_1-derivatives of which with aq. $Pb(OH)_2$ yield orthosaccharic acid (I) (*phenylhydrazide*, m.p. 176°; Ac_4 derivative, m.p. 110°, and its *phenylhydrazide*, m.p. 143°). (I) and MeI–Ag_2O yield the *Me* ester, m.p. 81·5°, of *tetramethylorthosaccharic acid* (II), m.p. 92—94° (*phenylhydrazide*, m.p. 113°), obtained by hydrolysing the ester with aq. $Ba(OH)_2$. Glucal and MeI–Ag_2O yield 3 : 4 : 6-trimethylglucal, which is chlorinated in $CHCl_3$ to 1 : 2-*dichloro*-3 : 4 : 6-*trimethylglucal*, an oil, converted by shaking with Ag_2CO_3 into the 2-*Cl*-derivative, an oil, and this yields trimethylorthosaccharic acid (III) when warmed with aq. $Pb(OH)_2$. (III), MeI, and Ag_2O afford (II). R. T.

Photo-decomposition of acetone.—See this vol., 1077.

Preparation of β-chloroethyl and β-vinyl ketones. J. Décombe (Compt. rend., 1936, **202**, 1685—1687; cf. A., 1907, i, 241, 418; 1908, i, 390, 398).—$COMe_2$, COMeEt, and $COEt_2$ with CH_2O in presence of K_2CO_3 (cf. A., 1933, 1144) afford α-hydroxybutan-γ-one (I), β-hydroxymethylbutan-γ-one (II), and β-*hydroxymethylpentan-γ-one* (III), b.p. 97—98°/20 mm. (*phenylhydrazone*, m.p. 103°), respectively. (I), (II), and (III) in conc. HCl containing some $AlCl_3$ at 0° afford α-chloro-, β-*chloromethyl-butan-γ-one*, b.p. 60—62°/16 mm., and β-*chloromethylpentan-γ-one*, b.p. 65—66°/14 mm., respectively, which are unstable in air, and by distilling in presence of a little (I) give Δ^a-buten-γ-one, β-*methyl*-Δ^a-*buten-γ-one*, b.p. 29—31°/60 mm. (*oxime*, m.p. 43°), and β-*methyl*-Δ^a-*penten-γ-one*, b.p. 119—120° (*semicarbazone*, m.p. 158°), respectively. J. L. D.

Utilisation of molecular refraction for determining constitution and configuration of sugars. I. C. N. Riiber (Z. physikal. Chem., 1936, **176**, 358—362).—The mol. refraction of a methyloside is > that of the corresponding sugar by 7·50±0·02 (ΔR_a) or 4·61±0·02 (ΔR_L). R. C.

Reduction and oxidation by ultra-violet irradiated sugar. P. Holtz (Arch. exp. Path. Pharm., 1936, **182**, 141—159).—Irradiation (especially in presence of O_2) of glucose, fructose, arabinose, glycerol, sorbitol, and glucosamine produces reducing substances, the resulting solutions (in common with those of ascorbic acid, reductone, and sugar heated with alkali) having absorption max. between 265 and 290 mμ; probably readily-enolised ·CO· is formed. The products accelerate the autoxidation of cysteine and adrenaline. The bearing of the data on biological reducing systems and the possibility of a similar formation from irradiation of the skin are discussed. F. O. H.

Action of *X*-rays on glucose. P. Holtz and J. P. Becker (Arch. exp. Path. Pharm., 1936, **182**, 160—163).—*X*-Irradiation of glucose (I) in PO_4''' buffer at p_H 7·6 yields solutions which reduce methylene-blue and have an absorption max. at 275—290 mμ, *i.e.*, similar to that of ultra-violet-irradiated (I) or of (I) heated in alkaline solution (cf. preceding abstract). F. O. H.

Action of dilute alkalis on glucose. I. R. Nodzu and R. Goto (Bull. Chem. Soc. Japan, 1936, **11**, 381—385).—The distillate of a dil. Na_2CO_3 solution of glucose is shown to contain acetol and a little Ac_2 but no COMe·CHO. Results are confirmed by spectroscopic evidence. A. T.

Acid–base catalysis of mutarotation of glucose.—See this vol., 1075.

Syntheses with 5 : 6-anhydro*iso*propylideneglucose. III. 6-Glucosylpiperidine. H. Ohle, E. Euler, and W. Malerczyk (Ber., 1936, **69**, [*B*], 1636—1639).—5 : 6-Anhydro*iso*propylideneglucose (I) gives mainly monoglucosylamine when treated with a large excess of amine in the cold. In EtOH much by-product, apparently formed by polymerisation of (I), results when the reactants are used in equimol. amount, but the proportion recedes with increasing amount and increasing concn. of amine. The following are described: iso*propylidene*-6-d-*glucosyl-methylamine*, b.p. 200—210° (bath)/0·15 mm., and *-dimethylamine*, m.p. 85°, $[\alpha]_D^{19}$ +8·7° in $CHCl_3$, *-ethylamine*, b.p. 190—200° (bath)/0·15—0·2 mm., m.p. 86°, $[\alpha]_D^{21}$ −8·5° in $CHCl_3$, and *-diethylamine*, b.p. 120—125° (bath)/0·05 mm., $[\alpha]_D^{22}$ +10·5° in $CHCl_3$; *-benzylamine*, b.p. 275° (bath)/0·05 mm., m.p. 109·5°, $[\alpha]_D^{20}$ −2·6° in $CHCl_3$, and *-dibenzylamine*, m.p. 133°, $[\alpha]_D^{21}$ +1·5° in $CHCl_3$. iso*Propylidene*-6-d-*glucosylpiperidine* (II), m.p. 115°, $[\alpha]_D^{21}$ +2·8° in $CHCl_3$ [*flavianate*, $C_{14}H_{25}O_5N,C_{10}H_6O_8N_2S,0{\cdot}5H_2O$, m.p. 115—117° (decomp.); *diacetate*], does not condense with $COMe_2$ in presence of anhyd. $CuSO_4$ or conc. H_2SO_4. *iso*Di*iso*propylideneglucose 6-*p*-toluenesulphonate and piperidine at 100° afford iso*di*iso*propylidene*-6-d-*glucosylpiperidine*, b.p. 155°/0·2 mm., $[\alpha]_D^{19}$ +32·37° in $CHCl_3$ [*monoflavianate*, m.p. 75° (decomp.)], hydrolysed by 0·05*N*-H_2SO_4 at 50° to (II), thus establishing the position of the piperidine residue at 6. Hydrolysis of (II) by *N*-H_2SO_4 at 20° gives β-6-d-*glucosylpiperidine*, m.p. 150—151° (decomp.), $[\alpha]_D^{22}$ +47·3° in H_2O (equilibrium val.), which could not be condensed with $COMe_2$ in presence of anhyd. $CuSO_4$. It gives a *phenylosazone*, m.p. 131°, and is acetylated predominatingly to the β-*tetra-acetate*, m.p. 134°, $[\alpha]_D^{22}$ +13·4° in $CHCl_3$. H. W.

Molecular transformation of *N*-glucosides. R. Kuhn and A. Dansi (Ber., 1936, **69**, [*B*], 1745—1754; cf. Amadori, A., 1926, 60; 1929, 429; 1931, 1039, 1149).—The "labile" compound ,m.p. 114—115°, $[\alpha]_D^{16}$ −92·5° to −35·5° in EtOH, obtained from glucose and *p*-$C_6H_4Me{\cdot}NH_2$ in boiling EtOH, is β-p-*toluidino*-d-*glucopyranoside* (I), since it is converted by Ac_2O in C_5H_5N into the tetra-acetate, m.p. 143—146°, $[\alpha]_D^{20}$ −57·5° in MeOAc, identical with that derived from *p*-$C_6H_4Me{\cdot}NH_2$ and acetobromoglucose or *d*-glucose 2 : 3 : 4 : 6-tetra-acetate. It is transformed by Me_2SO_4 into 2 : 3 : 4 : 6-tetramethyl-*p*-toluidinoglucose, m.p. 147°, $[\alpha]_D^{22}$ +163° in MeOH, identical with the product from *p*-$C_6H_4Me{\cdot}NH_2$ and 2 : 3 : 4 : 6-tetramethylglucose. The "stable" isomeride (II), m.p. 150—152°, $[\alpha]_D^{19}$ −40° in H_2O, cannot be methylated similarly, since it is unstable towards alkali. Treatment with Ag_2O and MeI gives *p*-$C_6H_4Me{\cdot}NHMe$ as sole cryst. product. With BzCl it affords a *tetrabenzoate*, m.p. 119—120°, instead of the pentabenzoate required by Amadori's formulation of it as a Schiff's base. Catalytic hydrogenation (PtO_2 in EtOH) readily gives the H_2-derivative $C_{13}H_{21}O_5N$, m.p. 195°, $[\alpha]_D^{23}$ +26° in C_5H_5N, +25° in *N*-HCl, not identical with *N*-*p*-tolylglucosamine. Attempts to prepare an undoubted Schiff's base from *al*-glucose 2 : 3 : 4 : 5 : 6-penta-acetate and *p*-$C_6H_4Me{\cdot}NH_2$ gave only gummy products. Oxidation of (II) with CrO_3 affords about twice as much AcOH as is obtained from (I) or *p*-$C_6H_4Me{\cdot}NH_2$, showing that isomerisation is accompanied by the production of a fresh Me which must be in the sugar residue, since (II) gives *p*-$C_6H_4Me{\cdot}NH_2$ when hydrolysed. In view of the possibility that (II) is the *p*-toluidide of a sugar carboxylic acid the following compounds have been prepared, none of which is identical with (II): *saccharin*-p-*toluidine*, m.p. 178—178·5°; *deoxyglucono*-p-*toluidide*, m.p. 176°, $[\alpha]_D^{20}$ +10° in C_5H_5N; d-*glucono*-p-*toluidide*, m.p. 179°, $[\alpha]_D^{14}$ +15·9°; p-*toluidino-2-deoxyglucose*, m.p. 192° (decomp.), $[\alpha]_D^{20}$ −67·5° to +10·0° in 48 hr. in EtOH–H_2O (1 : 1) or $[\alpha]_D^{21}$ +42·5° after addition of 2 drops of conc. HCl. The great reactivity of the *N*-glucosides is illustrated by the conversion of (I) by 4-nitro-5-amino-*o*-xylene into 4-*nitro-5-amino*-o-*xylyl*-d-*glucoside*, m.p. 213° (decomp.), $[\alpha]_D^{22}$ +54·6° in EtOH–H_2O (4 : 1), 0·0° in C_5H_5N. H. W.

Glycosides of madder. R. Hill and D. Richter (Nature, 1936, **138**, 38).—The glycoside obtained from various species of *Galium* and *Rubia* is the primveroside of purpurincarboxylic acid. The glycoside of alizarin has been cryst. from the products of enzymic hydrolysis and identified as primverose, and a primveroside of rubiadin has been obtained from the roots of *G. verum*. L. S. T.

Saponins of the *cyclo*pentanohydrophenanthrene group. V. Tigonin. R. Tschesche (Ber., 1936, **69**, [*B*], 1665—1668).—Treatment of the mother-liquors obtained after the isolation of lanadigin from the leaves of *Digitalis lanata* with cholesterol affords *cholesterol tigonide*, $C_{56}H_{92}O_{27},C_{27}H_{46}O$ (+4H_2O and +5H_2O), gradual decomp. >200°, transformed by C_5H_5N into *tigonin* (I), $C_{56}H_{92}O_{27}$ (also +1H_2O), m.p. 260° after softening at 220°. (I) is hydrolysed by H_2SO_4 to galactose, glucose, and xylose (2 : 2 : 1-mol.). Since tigogenin has only 1 OH at C_3 the sugar mols. must be united thereto, probably as a chain. (I) is less suitable than digitonin as a pptg. agent for sterols. H. W.

Saponins and sapogenins. IV. Isolation of amolonin and determination of hydrolysis products. P. C. Jurs and C. R. Noller (J. Amer. Chem. Soc., 1936, **58**, 1251—1255).—Details are given for the isolation of *amolonin* (I), $C_{63}H_{87}O_{14}(OH)_{17}$, $[\alpha]_{546}^{23}$ −75·5° in C_5H_5N (*Ac_{17}* derivative, $[\alpha]_{546}^{20}$ −33·53° in C_5H_5N), from the bulbs of *Chlorogalum pomeridianum*, Kunth. (I) is hydrolysed (50% aq. MeOH containing 5% H_2SO_4) to tigogenin, $C_{27}H_{43}O_2(OH)$ (1 mol.), *d*-glucose (3 mols.), *d*-galactose (1 mol.), and *l*-rhamnose (2 mols.). Chlorogenin is $C_{27}H_{42}O_2(OH)_2$ (cf. A., 1935, 673). H. B.

Mannans. III. Constitution of salep-mannan. Other carbohydrates of *Tubera salep*. F. Klages and R. Niemann (Annalen, 1936, **523**, 224—234; cf. A., 1934, 1093).—*T. salep* contains H_2O 12, ash 1·5, and insol. matter 3%. H_2O removes 30% of salep-mannan (I) and 13% of a dextrin, composed of varying amounts of glucose and mannose. 5% NaOH then removes 31% of starch, and finally $CuSO_4$–NH_3 removes 2% of cellulose. (I) is proved by methylation and hydrolysis to consist of mannose units joined in the 1 : 4 positions. The max. mol. wt. (yield of tetramethylglucose) is 12,000, the min. (f.-p. depression of C_6H_6) 5600. (I) closely resembles mannan-*A* and -*B* from ivory nut in solubility, rate of hydrolysis, [α], and [α] of derivatives. The viscosity of mannans is unusually low. Probably the mols. are joined together (*e.g.*, bridged by CH_2O) to give the rigid natural structures. R. S. C.

Fructose anhydrides. XVII. Constitution of sinistrin. H. H. Schlubach and W. Loop (Annalen, 1936, **523**, 130—143).—Expression of the bulbs of *Scilla maritima* and purification of the extract with basic $Pb(OAc)_2$ and H_2S followed by pptn. of the carbohydrates with EtOH yields sinistrin (I), $[\alpha]_D^{20}$ $-44.5°$ in H_2O, the homogeneity of which is established by its identity in [α], half period of acid hydrolysis, and mol. size in H_2O with a specimen obtained by hydrolysis (Zemplén) of the optically homogeneous *triacetate* (II), $[\alpha]_D^{20}$ $-23.5°$. (I) is a white hygroscopic powder which rapidly becomes a syrup when exposed to air. It contains 0·11% of ash. It does not reduce Fehling's solution. It decomposes at about 215° after softening at 170°, but degradation is obvious after some hr. at 60°. Acid hydrolysis effects 94·4% fission according to reducing power and 88·5% fission according to [α]. The maximal aldose val. (Auerbach–Bodländer) is 1·8%. Since reversion and simultaneous formation of furfuraldehyde derivatives inhibit the complete hydrolysis of polyfructosans and a similar small aldose val. is observed with other fructosans, it is concluded that (I) is formed exclusively of fructose units. The formation of an optically inactive reducing sugar could not be confirmed. (II) is readily methylated in $COMe_2$ according to Haworth to non-cryst. *methylsinistrin*, $[\alpha]_D^{20}$ $-57.0°$ in $CHCl_3$, which retains solvent very obstinately. It is hydrolysed by successive treatments with $H_2C_2O_4$–EtOH and 0·25% HCl and the product is treated with MeOH–HCl and benzoylated, whereby the following are isolated: *pentamethylfructose*, b.p. 66°/0·01 mm., $[\alpha]_D^{20}$ $+62.0°$, hydrolysed to 1 : 3 : 4 : 6-tetramethylfructose, b.p. 74°/0·01 mm.; *trimethylmethylfructoside benzoate*, b.p. 130°/0·01 mm., converted into a *trimethylmethylfructoside*, b.p. 77°/0·01 mm., and thence into a trimethylfructose, b.p. 90°/0·01 mm., $[\alpha]_D^{20}$ $+19.2°$ to $+13.7°$ in $CHCl_3$, $+5.8°$ to 0° in H_2O, which gives the osazone of 3 : 4 : 6-trimethylfructose in small amount, but is probably a mixture of isomerides; *dimethylmethylfructoside dibenzoate* giving a *dimethylmethylfructoside*, b.p. 92°/0·01 mm., and thence a *dimethylfructose*, b.p. 132°/0·01 mm., $[\alpha]_D^{20}$ $-6.8°$ in $CHCl_3$, $[\alpha]_D^{20}$ $-45.2°$ to $-54.6°$ in H_2O, $-19.3°$ to $-23.7°$ in abs. MeOH, which yields a *monomethylfructosazone*, m.p. 202°. The ratio of di- : tri- : tetra-methylfructose appears to be 1 : 3 : 1. H. W.

Enzymic degradation of starch. J. Blom, A. Bak, and B. Braae (Z. physiol. Chem., 1936, **241**, 273—287).—The limit of hydrolysis of starch (I) by α-amylase (II) is at 47%; there are checks at 33% and 40%. The limit for purest β-amylase (III) [(II) destroyed by AcOH at 0° and p_H 3·6] is 53·1±0·5%, this val. being independent of the concn. of (III) and of the presence of maltose, and the limit for (II)+(III) is 80·1±0·4%. Very high concns. of malt amylase (free from maltase but containing complement) convert (I) quantitatively into disaccharides and amylase from *Aspergillus oryzæ* converts (I) quantitatively into monosaccharides. The capability to give the "starch–iodide" reaction is destroyed partly by (III) and wholly by (II). These results and the properties of the dextrins produced at the different stages of hydrolysis indicate that the disaccharide residues in (I) are united by four different types of linking which exhibit unequal resistance to attack. The (I) mol. is probably made up of 30*n* monosaccharide or 15*n* disaccharide residues. W. McC.

Nature of cellulose. E. Heuser (Amer. Dyestuff Rep., 1936, **25**, 55—60, 80—83, 116—120, 135—137, 315—318, 338—339).—A review. A. J. H.

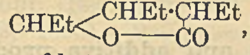
Cellulose as a highly polymerised compound. K. Freudenberg (Ber., 1936, **69**, [*B*], 1627—1631).—A historical account of the conception of cellulose as a highly polymerised compound. H. W.

Action of metallic sodium on cellulose. P. Schorigin and N. N. Makarova-Semljanskaja (Ber., 1936, **69**, [*B*], 1713—1721).—Examination of the action of Na in liquid NH_3 on cellulose shows that all its 3 OH groups participate in the change. There is no marked difference in the reactivity of the individual OH groups and the product is stable to Na. The individual Na atoms are united with different firmness, as shown by the marked partial alcoholysis of the Na_3 derivatives; probably this is due mainly to the heterogeneous structure of cellulose. Only about one third of the ONa groups are active towards MeI, and the methylcellulose produced is a mixture of products in which the no. and position of the Me vary. During attempts to establish the presence of free OH at 6 it is shown that re-etherification does not occur during the action of CPh_3Cl on methylcellulose. The interaction of Na_3 cellulose and CS_2 is very sluggish and the products have a very low sap. val. The alkoxy-structure of "soda cellulose" is confirmed, since its reactions are similar in principle to those of Na_3 cellulose. H. W.

Selenium-substituted amino-acids. I. Synthesis of αα′-diamino-ββ′-diselenodipropionic acid (selenocystine). A. Fredga (Svensk Kem. Tidskr., 1936, **48**, 160—165).—Interaction of $CH_2Cl\cdot CH(NH_2)\cdot CO_2Me,HCl$ with K_2Se_2 in alkaline medium at room temp. and subsequent evaporation gives *αα′-diamino-ββ′-diselenodipropionic acid* (I), two forms, rectangular plates, m.p. about 215° (decomp.) after becoming grey at about 180°, and rhombic plates (*r*- and *meso*-isomerides) (*Cu* salt). (I) is transformed by Hg in acid solution followed by Na_2S and CH_2PhCl in alkaline solution into *benzylselenolcysteine*, $C_{10}H_{13}O_2NSe,H_2O$, m.p. about 185° (decomp.) after softening at 150°. H. W.

New type of hypnotic amide. Diethylacet-β-ketopropylamide. W. A. Lott and W. G. Christiansen (J. Amer. Pharm. Assoc., 1936, **25**, 310).—$CHEt_2\cdot COCl$ with C_5H_5N (in C_6H_6) yields the mol. compound, which with aminoacetone hydrochloride affords the above *amide*, m.p. 96—97°, having no pronounced hypnotic activity. F. O. H.

Action of magnesium ethyl bromide on butyrethylanilide. M. Montagne and Y. Isambert (Compt. rend., 1936, **203**, 331—333).—The action of MgEtBr on butyrethylanilide (I) in boiling Et_2O

or PhMe gives considerable amounts of C_2H_6, $CEt_2Pr^a{\cdot}OH$, and β-*hydroxy*-αβ-*diethylhexethylanilide* (II), b.p. 155—157°/3 mm. (II) passes when distilled under atm. pressure or boiled with NaOH–EtOH into $COEtPr^a$ and (I) and is hydrolysed by boiling 48% HBr to NHPhEt and neutral products, including δ-*ethyl*-Δ$^\delta$-*heptene*, b.p. 138—145°/760 mm. (*dibromide*, b.p. 95—100°/20 mm.), and a *lactone*  $CPr^a{<}\begin{matrix}CHEt{-}CO\\CHMe{\cdot}O\end{matrix}$ or  $CHEt{<}\begin{matrix}CHEt{\cdot}CHEt\\O{-\!-\!-}CO\end{matrix}$, b.p. 132°/18, mm. The formation of ketone or *tert*. amine as from HCO·NPhEt or $HCO{\cdot}NEt_2$ is scarcely observed.

H. W.

Transformation of carbamide into ammonium carbonate. E. Toporescu (Compt. rend., 1936, **202**, 2075).—2% aq. $CO(NH_2)_2$, placed in the inner cell of a parchment dialyser, with 6% aq. NaCl in the outer compartment, was partly converted into $(NH_4)_2CO_3$ in 24 hr. at 40°.

H. J. E.

Oxidation products of thiocarbamide. The dioxide as derivative of sulphoxylic acid. J. Böeseken (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 717—721).—$CS(NH_2)_2$ in 50% EtOH with slightly more than the calc. amount of an acid and ½ mol. of H_2O_2 affords salts of dithioformamidine (I). $CS(NH_2)_2$ in neutral solution with H_2O_2 or AcO_2H affords *thiocarbamide dioxide* (II) and not, as suggested by Barnett (J.C.S., 1910, **97**, 63), formamidinesulphinic acid. It is neutral to litmus and to Congo-red, and is a strong reducing agent, pptg. many metals from solutions. Dil. NaOH reacts to form $Na_2S_2O_3$, and $Ba(OH)_2$ affords $BaSO_4$ and $CO(NH_2)_2$. With AcO_2H, (II) affords *formamidinesulphonic acid* (III), also obtainable from $CS(NH_2)_2$ and 3 mols. of AcO_2H, whereas AcO_2H in presence of $NaNO_3$ and AcOH converts $CS(NH_2)_2$ into the nitrate of (I). (III) does not react with cold, acid $KMnO_4$ solution, but $Ba(OH)_2$ affords $BaSO_3$ and $CN{\cdot}NH_2$. No experimental details are given.

P. G. C.

(A) Hydrazides, (B) azides, of unsaturated fatty acids. (C) Hydrazides and azides of naphthenic acids. A. Oskerko (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, **2**, 69—77, 79—92, 293—302).—(A) The *hydrazides* of oleic acid (I), m.p. 95—96° (*hydrochloride*, m.p. 110—112°), erucic acid (II), m.p. 77—78° (*hydrochloride*, m.p. 120—121°), and undecenoic acid (III), m.p. 84—85° (*hydrochloride*, m.p. 128—130°), are obtained by boiling the Me esters of the appropriate acids with N_2H_4,H_2O.

(B) The *azides* of (I), (II), and (III), prepared from the above hydrochlorides and aq. $NaNO_2$, or from the acid chlorides and NaN_3 in $COMe_2$, are oils, readily decomp. at room temp. to yield carbimides; when boiled with EtOH they yield respectively the *urethane* of (I), m.p. 42—43°, of (II), m.p. 47—48°, and of (III), m.p. 53—54°.

(C) The *hydrazide*, m.p. 28—29° (*hydrochloride*, m.p. 157—159°), and *azide* (IV), an oil, of decahydronaphthoic acid (V) have been prepared by the above methods. (IV) decomposes at room temp. to yield the *carbimide*, b.p. 194—196°/7 mm., of (V), the *urethane*, b.p. 84—86°/3 mm., of which is obtained by boiling with EtOH. Gaseous or aq. NH_3 converts (IV) into the amide of (V).

R. T.

Complex compounds of dicarboxylic acid hydrazides.—See this vol., 1078.

Reaction of semicarbazones with alcohols. E. W. McClelland and C. E. Salkeld (J.C.S., 1936, 1050).—*iso*-$C_5H_{11}{\cdot}OH$ and the aldehyde or ketone semicarbazone react with elimination of NH_3 to give iso*amyl benzylidene*-, m.p. 103°, α-*phenylethylidene*-, m.p. 74°, o-*hydroxybenzylidene*-, m.p. 140°, *piperonylidene*-, m.p. 83°, and o-*nitrobenzylidene-hydrazinecarboxylate*, m.p. 95°.

F. R. S.

Organo-arsenic compounds. III. H. N. Das-Gupta (J. Indian Chem. Soc., 1936, **13**, 305—308).—$AsMeCl_2$ and C_2H_2 give methyl-ββ-dichlorovinylarsine and *methyl*-β-*chlorovinylchloroarsine*, b.p. 110—115°, which with H_2O_2 affords *methyl*-β-*chlorovinylarsinic acid*, m.p. 149—150°, with MgPhBr yields *phenylmethyl*-β-*chlorovinylarsine*, and with the appropriate reagents forms *methyl*-β-*chlorovinylarsenious sulphide*, *cyanide*, and *oxide*.

F. R. S.

Resolution of α-arsino-carboxylic acids. H. J. Backer and C. H. K. Mulder (Rec. trav. chim., 1936, **55**, 594—601).—d-α-*Arsino-propionic*, -*butyric*, -*valeric*, -*hexoic*, -*heptoic*, -*octoic*, -*nonoic*, and -*phenylacetic acids* (I), m.p. 134°, 127°, 116—117°, 96°, 82—83°, 114°, and 115°, $[M]_D$ +41°, +25·7°, +19·3°, +6·1°, +21·9°, +3°, +3·4°, and +3·1° in H_2O, respectively, are obtained from the *dl*-acids by way of the *diquinine* salts, +6, 5, 4, 3, 2, 5·5, 5, and $6H_2O$, respectively. The *Ba H* salts have $[M]_D$ −8·5°, −10·5°, −15·7°, −8·2°, −19·4°, −5°, −7·5°, and +4·2° in H_2O, respectively, there being an inversion in all except the last case; addition of a third equiv. of Ba has little effect. The Ba salts, except that of (I), do not racemise. The free acids racemise slowly [(I) fast], slightly faster in presence of HCl.

R. S. C.

Polymetatelluric acid esters. M. Patry (Compt. rend., 1936, **202**, 2088—2090).—MeOH, EtOH, and Pr^aOH dissolve hydrated TeO_3 in the cold. Bu^aOH and $C_5H_{11}{\cdot}OH$ dissolve it on heating. By refluxing and evaporating a residue is obtained from which the normal esters $(TeO_4R_2)_n$ can be extracted with Et_2O (except in the case of MeOH). *sec.* and *tert.* saturated alcohols do not react with polymetatelluric acid, but glycerol and $CH_2Ph{\cdot}OH$ readily yield esters. The properties of polymetatelluric esters (I) are reviewed. Orthotelluric acid dissolves slowly when heated with MeOH, EtOH, PrOH, BuOH, and $C_5H_{11}{\cdot}OH$. Evaporation of the solution yields (I). A solution of CH_2N_2 in Et_2O with hydrated TeO_3 yields the normal ester, $TeMe_2O$, on evaporation.

H. J. E.

Formation of organo-magnesium halides and their behaviour towards halogen acids, their ammonium and amine salts, and towards aniline. J. Houben, J. Boedler, and W. Fischer (Ber., 1936, **69**, [*B*], 1766—1788).—The use of Mg powder in the prep. of Grignard reagents is not generally advisable, since when preserved it readily absorbs H_2O and is partly converted into MgO and $Mg(OH)_2$, whereby ultimately the Würtz–Fittig synthesis is facilitated; if used, it should be freshly filed from a Mg block, but does not then exceed

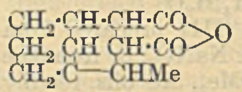
Mg turnings in activity, particularly if the latter are freshly triturated in a warm mortar. In the complete absence of air and moisture (presence of Na) in the alkyl halide series C_1 to C_{16} the mean yields of MgAlkHal are 97·6%, 89·6%, and 85·8%, respectively, in the cases of chloride, bromide, and iodide. The min. yield of 79·7% is observed in the case of Mg cetyl iodide. Grignard's observation that the Würtz–Fittig synthesis predominates when C is >6 is therefore erroneous under these conditions. Contrary to Hess *et al.* (A., 1921, i, 777), MgEtI is completely decomposed by HBr, although, under some conditions, only partly by HI; if excess of the latter is used, complete decomp. of MgEtI and all other Grignard reagents, whether "individual" or in Et_2O, is achieved. A ready prep. of HBr or HI from Br or I and boiling tetrahydronaphthalene is described. Only MgEtI (and possibly MgMeI) is smoothly decomposed by NH_4Cl, NH_4Br, and NH_4I, whereas NH_4F is without action. NH_4Cl and NH_4Br are inactive towards MgEtCl and MgEtBr, whereas both are decomposed by NH_4I. Possibly the difference is due to the differing solubility of the NH_4 salts in the Grignard solutions and depends somewhat on their state of division. NH_2Me,HCl is only slightly more active than NH_4Cl. NEt_3,HCl is more active, whereas NEt_4I is completely ineffective even in presence of $FeCl_3$. NH_2Ph,HCl is as vigorous as NH_2Ph in its action on MgEtCl. With mixtures of Grignard reagents a difficultly explicable inactivation is observed. The apparent inertia of a mixture of NHPh·MgI and MgMeI towards CO_2 in a closed vessel (Houben, A., 1905, i, 873) is caused by the liberation of an equal vol. of CH_4 thus: $NHPh{\cdot}MgI + MgMeI + CO_2 = MgMeI + NHPh{\cdot}CO_2MgI = MgI{\cdot}NPh{\cdot}CO_2MgI + CH_4$. H. W.

Complex compounds of the olefines with metallic salts. II. Homologues of Zeise's salt. J. S. Anderson (J.C.S., 1936, 1042—1049).—The formation of compounds of $PtCl_2$ with olefines has been shown to be effected by the reactions (*a*) displacement of Cl′ from $PtCl_2$ anion and (*b*) displacement of one olefine from such complexes by another olefine. By this reaction, compounds analogous to ethylene Pt chloride (I) may be obtained and evidence is advanced that bis-olefine compounds may exist. Reaction (*b*) affords conclusive evidence that the attachment of the olefines is truly co-ordinative, and not by principal valencies. The co-ordinating ability decreases in the order C_2H_4 > CHPh:CH_2 > indene > *cyclo*hexene > CPh_2:CH_2 and CPhMe:CH_2, and this is discussed in relation to steric and polar influences on the double linking. With K_2PtCl_4, styrene gives K styrenetrichloroplatinite, which with tetramminoplatinous chloride forms *tetramminoplatinous styrenechloroplatinite*, whilst indene yields *K indenetrichloroplatinite*, converted by $[CoCl_2\,en_2]Cl$ into 1 : 6-*dichlorobisethylenediaminocobaltic indenetrichloroplatinite*. *cyclo*Hexene with EtOH–H_2PtCl_4 gives a complex, which with $[CoCl_2\,en_2]Cl$ yields 1 : 6-*dichlorobisethylenediaminocobaltic* cyclo*hexenetrichloroplatinite*. Styrene with Zeise's salt gives *K styrenetrichloroplatinite*, and with (I) forms *distyreneplatinous chloride*. Δ^β-Amylene with (I) yields *amyleneplatinous chloride*. Anilinium carbonyltrichloroplatinite does not react with styrene. F. R. S.

Contact transformation of *cis*- and *trans*-dimethyl*cyclo*hexane. E. I. Margolis (Ber., 1936, 69, [*B*], 1710—1713).—With *o*-, *m*-, and *p*-dimethyl*cyclo*hexane passage over Os–asbestos at 50—70° does not cause isomerisation of the *trans*- into the *cis*-form. H. W.

Addition and additive products of halogens to benzene derivatives. VII. Addition of chlorine to penta- and hexa-chlorobenzene. T. van der Linden (Rec. trav. chim., 1936, 55, 569—576; cf. this vol., 975).—C_6HCl_5 and liquid Cl_2 in light give (5 months) mainly mixed crystals (I), m.p. 90—92°, of 1 : 2 : 3 : 3 : 4 : 4 : 5 : 6 : 6-*nonachloro*-Δ^1-cyclo*hexene* (91·5%) and an isomeride thereof (8·5%) with a little C_6Cl_6 [probably produced by loss of Cl from (I), less probably by direct substitution]. The nature of (I) is determined by quant. reaction with Zn–EtOH to C_6HCl_5 and with NaOH–MeOH to much C_6Cl_6 and a little octachloro-$\Delta^{2:5}$-*cyclo*hexadiene (II). C_6Cl_6 and an excess of liquid Cl_2 in light give (3 months) *dodecachloro*cyclo*hexane* (III), sublimes from 250°, m.p. about 285° (decomp. with liberation of Cl_2; sealed tube), not volatile in steam, almost odourless, and stable to fuming HNO_3. C_6Cl_6 and $3Cl_2$ give very slowly (III) and *decachloro*cyclo*hexene* (IV), m.p. about 92°. (III) and (IV) react only slowly with NaOH–EtOH. The substance, m.p. 66—68°, of Smith *et al.* (A., 1934, 40) is not (III); it may be a stereoisomeride (chair–boat forms), but this is improbable. Addition of Cl_2 probably occurs first at CH:CCl and then mainly at the ends of the conjugated system of ethylenic linkings thus produced. *cyclo*Hexadienes with conjugated linkings are too unstable to exist. The preferential formation of certain isomerides by addition of Cl_2 to C_6H_6 and its derivatives probably depends on energy relations. (II) is the only Cl-derivative in this series to lose HCl to Zn–EtOH. R. S. C.

Isomerisation of cyclic hydrocarbons with isolated systems of double linkings. J. M. Slobodin (J. Gen. Chem. Russ., 1936, 6, 129—136).—1-Vinyl-Δ^3-*cyclo*hexene when heated at 200—235° in presence of floridin is converted into 1-*vinyl*-Δ^2-cyclo*hexene* (I), b.p. 130—137°, yielding 1-α-*hydroxyethyl*-1 : 2 : 3-*trihydroxy*cyclo*hexane* (II), m.p. 48°, on oxidation with $KMnO_4$ at 0°. (II) yields α-ketoadipic acid with $K_2Cr_2O_7$ and H_2SO_4 in H_2O (at the b.p.). (I) with maleic anhydride at 100° affords (III). *d*-Limonene at 210—235° in presence of floridin yields chiefly *iso*limonene. R. T.



(III.)

Phenyl*cyclo*pentylmethane and *cyclo*hexyl*cyclo*pentylmethane and their behaviour during catalytic hydrogenation. J. I. Denissenko (Ber., 1936, 69, [*B*], 1668—1670).—*cyclo*Pentanone and $CH_2Ph{\cdot}MgCl$ yield 1-*benzyl*cyclo*pentan*-1-*ol*, b.p. 129—130°/11 mm., dehydrated by anhyd. $H_2C_2O_4$ to *phenyl*-Δ^1-cyclo*pentenylmethane*, b.p. 120—122°/10 mm., catalytically hydrogenated (Pt-black in EtOH) to *phenyl*cyclo*pentylmethane* (I), b.p. 234—236°/750 mm. When passed with H_2 over Pt–C at 190—200°, (I) gives cyclo*pentyl*cyclo*hexylmethane* (II), b.p. 224—226°/750 mm. Passage of (I) or (II) over Pt–C at 300—310° is accompanied by fission of the *cyclo*pentyl groups and gives mainly *n*-hexylbenzene. H. W.

Terpenoid ring systems. II. Polyionone. H. Vogel and M. Stohl (Ber., 1936, 69, [*B*], 1573—1575; cf. A., 1933, 1055).—Polyionone (improved prep.) is probably CRMe:CH·C(CH:CHR):CH·COR ($R{=}CH{:}CH{\cdot}C{<}\begin{smallmatrix}CMe_2{\cdot}CH_2\\ CMe{-}CH_2\end{smallmatrix}{>}CH_2$). It is readily autoxidised and must be preserved under N_2 in the dark. When its solution in Et_2O is placed over 25% HCl a bluish-violet zone is formed and after agitation the acid layer becomes dark violet, whilst the ethereal solution becomes lighter in colour. H. W.

Formation of carbon chains during the catalytic hydrogenation of alkyl halides. M. Busch and W. Weber [with C. Darboven, W. Renner, H. J. Hahn, G. Mathauser, F. Strätz, K. Zitzmann, and H. Engelhardt] (J. pr. Chem., 1936, [ii], 146, 1—55).—Under conditions similar to those adopted with Pd, Pt causes little elimination of Br from PhBr. Os, Ru, and Rh are similarly unsuitable. Kelber's Ni in presence of KOH–EtOH–H_2 is inactive; with N_2H_4 as source of H, however, the change is very rapid, and only with PhCl is Pd superior to Ni. The formation of Ph_2 is never observed. Diaryl production is not therefore due to intermediate radical formation, but is a sp. action of Pd. Since Ph_2 is produced only in min. amount from PhBr and Pd–$CaCO_3$ in H_2O in presence of H_2 or N_2H_4, a sp. action of MeOH (EtOH) is indicated, and when PhBr is heated in KOH–MeOH containing Pd–$CaCO_3$ Ph_2 is obtained in 15—20% yield which is not influenced by presence of H_2 or N_2H_4. H is derived therefore from MeOH, and, accordingly, CH_2O is detected in the solution. The initial reaction is therefore $PdH_2 + PhBr \rightarrow HBr + PdPhH$. In presence of active H in sufficient concn. the following step is $PdPhH + 2H \rightarrow PdH_2 + C_6H_6$, whereas in its absence reaction is $PdPhH + PhBr \rightarrow PdPh_2 + HBr$ and $PdPh_2 + H_2 \rightarrow PdH_2 + Ph_2$. The favourable influence of N_2H_4 on the yield of diaryl depends on its power of reaction with CH_2O to form $(CH_2)_2N_2$ which is ultimately reduced to NH_2Me, whereby the concn. of active H is diminished. As expected, an optimal concn. of N_2H_4 is observed. The hydrogenation of PhBr under widely varied conditions is described. With compounds C_6H_4XY (X=Cl or Br; Y=NH_2, NMe_2, Me, CO_2H, OMe, or OH), Cl is less readily eliminated than Br, and Cl-compounds are therefore less suitable for the production of diaryls. Little difference in the degree of diaryl formation is observed between *m*- and *p*-derivatives, whereas *o*-compounds are more difficult to hydrogenate and nuclear union is seldom observed. Loss of halogen increases with increasing concn. of N_2H_4, but greater production of diaryl is not general. *p*-$C_6H_4Br{\cdot}COMe$ in presence of N_2H_4 affords the azine and hydrazone of COPhMe and pp′-*diacetophenonedihydrazone*, decomp. 195—200°, which passes when preserved into the *diazine*, $CMe{<}\begin{smallmatrix}C_6H_4{\cdot}C_6H_4\\ N{=\!=\!=}N\end{smallmatrix}{>}CMe$ or $\begin{smallmatrix}N{:}CMe{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CMe{:}N\\ N{:}CMe{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CMe{:}N\end{smallmatrix}$, decomp. > 350°. 3-Bromopyridine affords C_5H_5N and 3 : 3′-dipyridyl. *p*-$C_6H_4Br_2$ affords Ph_2, *p*-$C_6H_4Ph_2$, and (*p*-$C_6H_4Ph{\cdot})_2$, isolated by extraction of the catalyst with suitable solvents, and p-*quinquiphenyl*, m.p. 395°, p-*sexiphenyl*, m.p. 475°, and p-*septiphenyl*, m.p. 545°, obtained by fractional sublimation under diminished pressure from the catalyst. Hydrogenation of *m*-$C_6H_4Br_2$ in presence of KOH–MeOH–H_2O–Pd–N_2H_4 at 140° yields m-*noniphenyl* $C_{54}H_{38}$, m.p. 166° after softening at 163°, m-*deciphenyl*, m.p. 184° after softening at 180°, m-*undeciphenyl*, m.p. 202° after softening at 195°, m-*duodeciphenyl*, m.p. 223° after softening at 214°, *trideciphenyl*, m.p. 245° after softening at 239° {*NO_2*-derivative, (?) $(NO_2)_3C_6H_2{\cdot}[C_6H_3{\cdot}NO_2]_{11}{\cdot}C_6H_2(NO_2)_3$, m.p. 185° (decomp.); *Cl*-derivative, $C_{78}H_{41}Cl_{13}$, m.p. 156° after softening at 152°}, whereas in boiling solution m-*quinquiphenyl*, m.p. 112°, with products composed of 11—14 nuclei and containing Br results. When *m*-$C_6H_4I_2$ is used the product is greatly contaminated with coloured materials. *o*-$C_6H_4Br_2$ gives C_6H_6, some Ph_2, and very little more complex material. 3 : 5-$C_6H_3MeBr_2$ yields 3 : 3′-ditolyl, m-*tritolyl*, $C_6H_3Me(C_6H_4Me)_2$, m.p. 65°, and a little more complex product. With phenols little chain formation is observed, whereas 2 : 4-$C_6H_3Br_2{\cdot}OMe$ gives PhOMe with considerable amounts of *pp*′- and some *oo*′-dianisole. 1 : 8-$C_{10}H_6Br_2$ affords $C_{10}H_8$, di- and tetra-hydronaphthalene, with indications of the presence of perylene, but analogous experiments with 1 : 8-$C_{10}H_6I_2$ are unsatisfactory. 1 : 6-Dibromo-2-naphthol gives β-$C_{10}H_7$-OH and 2 : 2′-dihydroxy-1 : 1′-dinaphthyl. 3 : 5-Dibromopyridine yields dipyridyl (30%), *terpyridyl* (18%), m.p. 249—251°, (?) *quaterpyridyl* (5%), m.p. 290° (*hydrochloride*; *perchlorate*), and (?) *quinquipyridyl* (2%), m.p. 330°. *s*-$C_6H_3Br_3$ yields highly complex *products*, m.p. 241° after softening at 235°, m.p. 259—261°, and m.p. 280—285°, respectively, probably containing 30, 16, and 22 C_6H_6 nuclei, respectively. *pp*′-Dibromodiphenylmethane affords 4 : 4′-*dibenzyldiphenyl*, m.p. 114—115°, *terdiphenylmethane*, m.p. 179—180° after softening at 175°, *quaterdiphenylmethane*, m.p. 239—240°, and (?) *quinquidiphenylmethane*, m.p. 280°. 2 : 2′-Dibromodiphenylmethane yields CH_2Ph_2 and fluorene (14% yield). 2 : 2′-Dibromo-5 : 5′-diaminodiphenylmethane gives 5 : 5′-diaminodiphenylmethane and diaminofluorene, m.p. 164° (yield 3·5%). Dihydrophenanthrene (yield about 30%) and $(CH_2Ph)_2$ are obtained from 2 : 2′-di-iododibenzyl. Under the usual conditions CH_2PhCl and CH_2PhBr afford PhMe and $({\cdot}CH_2Ph)_2$, but in very conc. solution CH_2PhCl affords $CH_2Ph{\cdot}O{\cdot}Et$ and $N(CH_2Ph)_2{\cdot}NH_2$. $CHPhCl_2$ gives $({\cdot}CHPhCl)_2$ further hydrogenated to stilbene. $CPhCl_3$ gives a mixture of α- and β-$({:}CPhCl)_2$ which also appears to be derived from $({\cdot}CPhCl_2)_2$. Drastic reduction of $({:}CPhCl)_2$ affords $({\cdot}CH_2Ph)_2$, also obtained from stilbene. *o*-$C_6H_4Cl{\cdot}CH_2Cl$ gives *o*-$C_6H_4Cl{\cdot}CH_2{\cdot}OMe$, whereas *p*-$C_6H_4Cl{\cdot}CH_2Cl$ affords *p*-$C_6H_4Cl{\cdot}CH_2{\cdot}OEt$ and $({\cdot}CH_2Ph)_2$. $({\cdot}CHPh_2)_2$ and $CHPh{\cdot}OMe$ result from $CHPh_2Br$. Phenyl*cyclo*hexylmethyl chloride gives αβ-*diphenyl*-αβ-*dicyclohexylethane*, m.p. 198—200°. $CHPhBr{\cdot}CO_2Et$ yields $({\cdot}CHPh{\cdot}CO_2H)_2$, but

$CH_2Cl\cdot CO_2H$ gives $OH\cdot CH_2\cdot CO_2H$. CHPh:CHBr affords diphenylbutadiene (and polymerides) which could not be hydrogenated further. H. W.

Nuclear-substituted derivatives of *iso*propylbenzene. W. Qvist and A. Salo (Acta Acad. Aboensis Math. Phys., 1934, **8**, No. 4, 30 pp.; Chem. Zentr., 1934, ii, 594—595).—The Pr^{β} group in $PhPr^{\beta}$ is more readily replaced by Cl than in *p*-cymene. Passage of Cl_2 into $PhPr^{\beta}$, in CCl_4 at 0° in presence of I in daylight, affords mainly 2 : 4 : 5-*trichlorocumene* (I), b.p. 240—245°, which with HNO_3 gives 2 : 4 : 5-trichloro-1 : 3-dinitrobenzene, m.p. 102·5—103·5°; this with $EtOH–NH_3$ yields 6-*chloro*-2 : 4-*dinitro*-m-*phenylenediamine*, m.p. 249—249·5°, and, with NH_2Ph, 6-*chloro*-2 : 4-*dinitro*-1 : 3-*dianilinobenzene*, m.p. 188°. (I) is accompanied by *p*-$C_6H_4Cl_2$; 1 : 2 : 4 : 5-$C_6H_2Cl_4$, m.p. 139·5—140·5°, yielding the 3-NO_2-, m.p. 99—100°, and 3 : 3-$(NO_2)_2$-, m.p. 232—233°, compounds, with HNO_3; 1 : 3 : 4 : 5-$C_6H_2Cl_4$ and C_6HCl_5. Passage of Cl_2 into $PhPr^{\beta}$ containing I and Fe at 0° in the dark affords *p*-chlorocumene (II), b.p. 190—200°, 3 : 4-*dichlorocumene* (III), b.p. 120—125°/9 mm., (I), b.p. 125—130°/9 mm., 2 : 4 : 5 : 6-*tetrachlorocumene* (IV), m.p. 41—41·5°, and 2 : 3 : 4 : 5 : 6-*pentachlorocumene* (V), m.p. 81—82°. (II) is oxidised to *p*-$C_6H_4Cl\cdot CO_2H$ and (III) to 2 : 4 : 5-$C_6H_2Cl_3\cdot CO_2H$, m.p. 164—165°. (IV) with HNO_3 yields 2 : 4 : 5 : 6-tetrachloro-1 : 3-dinitrobenzene, m.p. 153—154°, yielding 6-chloro-2 : 4-dinitro-1 : 3 : 5-trianilinobenzene, m.p. 179—180°, with NH_2Ph. (V) with HNO_3 yields $C_6Cl_5\cdot NO_2$, m.p. 144—145°, reduced to $C_6Cl_5\cdot NH_2$, m.p. 232—233°. Ch. Abs. (*r*)

Condensation of aryl methyl ketones. K. Bernhauer, P. Müller, and F. Neiser (J. pr. Chem., 1936, [ii], **145**, 301—308).—Condensation of ketones, COArMe, by $KHSO_4$ and a little H_2SO_4 to triarylbenzenes is favoured by the presence of negative and hindered by that of positive substituents in the Ar. COPhEt, $COPhPr^{\alpha}$, $COPhPr^{\beta}$, α- and β-$C_{10}H_7\cdot COMe$, and $COPh\cdot CH_2Ph$ (I) do not thus condense, presumably owing to steric hindrance. Yields are as stated, reaction being effected at 80—85° unless otherwise stated: *s*-$C_6H_3Me_3$ (37%; also obtained by I at 195° or in poor yield by HgI_2 at 240—250°); s-*tri*-p-*tolyl*-, m.p. 170° (14%), -p-*chlorophenyl*-, m.p. 238° (46%; also obtained by I at 170°), -m-*nitrophenyl*-, m.p. 298—299° (68%), -p-*diphenylyl*- (51% at 125°), m.p. 230—231°, and -p′-*nitro*-p-*diphenylyl-benzene*, m.p. 345—346° (32% at 160°). p-*Nitrophenyl-4-acetophenone*, m.p. 151°, b.p. 256—265°/10 mm., is obtained in 11% yield from *p*-$NO_2\cdot C_6H_4Ph$, AcCl, and $AlCl_3$ in $PhNO_2$ at 80°. (I) with I at 330—340° gives an 18% yield of s-*tetraphenylfuran*, m.p. 168·5—169° [identified by oxidation by $HNO_3–AcOH$ to $(CPhBz{:})_2$], probably by dehydrogenation of the intermediate $CH_2Ph\cdot CPh{:}CHPhBz$. R. S. C.

Dipole moments of certain polynitro-compounds.—See this vol., 924.

Chlorination of *p*-chlorotoluene. H. Wahl (Compt. rend., 1936, **202**, 2161—2163).—Direct chlorination of *p*-C_6H_4MeCl (20—40°; Fe catalyst) yields 1 : 2 : 4- (58%) and 1 : 3 : 4-$C_6H_3MeCl_2$ (42%). At 100° without catalyst, side-chain substitution occurs except in presence of $PbCl_2$, when normal nuclear substitution results. F. N. W.

Plano-radiate compounds. IV. Hexa(-chloro- and -iodo-methyl)benzene. H. J. Backer (Rec. trav. chim., 1936, **55**, 591—594; cf. this vol., 715).—$C_6(CH_2\cdot OH)_6$ (I) gives mixtures with $HCl–H_2SO_4$ and $SOCl_2$. Cl_2 and C_6Me_6 in boiling C_2HCl_5 give *hexa*(*chloromethyl*)*benzene*, m.p. 287·5° (crystallographic data given), converted by hot $KOAc–Ac_2O$ into $C_6(CH_2\cdot OAc)_6$. (I) and HI saturated at 0° give *hexa*(*iodomethyl*)*benzene*, decomp. from 200°. Hexa(alkylthiolmethyl)benzenes, $C_6(CH_2\cdot SR)_6$, give mixtures with $HgCl_2$; however, when R is Me, Et, or Bu^{a}, a *tetra*-, m.p. 100—102°, *octa*-, m.p. 98·5—99°, and *tetra-iodide*, m.p. 84·5°, respectively, are obtained. R. S. C.

Nitrosochlorides of the benzene series. R. Perrot (Compt. rend., 1936, **203**, 329—331).—When NOCl is added to the unsaturated aromatic compound dissolved in CCl_4 or $CHCl_3$ at a low temp. *nitrosochlorides* of the following compounds are obtained, frequently better characterised by converting them by piperidine in C_6H_6 into the corresponding *nitrolpiperidines*, the m.p. of which are recorded in parentheses: $CHPh{:}CH_2$, m.p. 102·5° (136°); *p*-tolylethylene, m.p. 101° (163·5°); CHPh:CHMe, m.p. 129·5° (115°); $CH_2{:}CHPhMe$, m.p. 89° (122°); CHPh:CHBr, m.p. 99—100° (162—163°); anethole, m.p. 126° (about 90°); $CPh_2{:}CH_2$, m.p. 95° (131°); $CHPh{:}CMe_2$, m.p. 121·5° (163°); CHPh:CHPh, m.p. 138° (155°); *cyclo*hexene, m.p. 150° (119°); 1 : 4-dihydronaphthalene, m.p. 143—144° (146°); indene, blackens at about 150° (157°); $COPh\cdot CH{:}CHPh$, m.p. 116° (about 60°). The mol. wt. of the compounds of each series determined cryoscopically in C_6H_6 or dioxan is 1·3—1·8 times as great as that expected. H. W.

Resolution of an allene hydrocarbon into optical antipodes by asymmetric catalysis. P. Maitland and W. H. Mills (J.C.S., 1936, 987—998).—β-*Hydroxy*-β-*phenyl*-β-1-*naphthylpropiophenone*, m.p. 167—169°, obtained from Mg, 1-$C_{10}H_7Br$, and CH_2Bz_2, is converted (HCl) into *Ph* β-*phenyl*-β-1-*naphthylvinyl ketone*, m.p. 107—108°, which with 1-$C_{10}H_7\cdot MgBr$ yields αγ-*diphenyl*-αγ-*di*-1-*naphthylallyl alcohol* (I), m.p. 187—189°. The ketone may also be prepared by dehydration (HCl) of α-*bromo*-β-*phenyl*-β-1-*naphthylpropiophenone*, m.p. 196—198°, obtained from 1-$C_{10}H_7\cdot MgBr$ and CHPh:CHBz. Dehydration of (I) with Ac_2O or *p*-$C_6H_4Me\cdot SO_3H$ affords r-αγ-*diphenyl*-αγ-*di*-1-*naphthylallene* (II), m.p. 242—244°. With *d*-camphor-β-sulphonic acid, (I) is dehydrated to a mixture of (II) and the d-*allene*, m.p. 158—159°, $[\alpha]^{17}_{5461}$ +437° in C_6H_6, and with the *l*-acid, the l-*allene*, m.p. 158—159°, $[\alpha]^{17}_{5461}$ −438° in C_6H_6, is obtained. The optically active allenes show great configurative stability and it is difficult to racemise them by heating. The configuration of (II) is confirmed by conversion with either AcOH and HCl or I into 1 : 3-*diphenyl*-1-1′-*naphthyl*-4 : 5-*benzindine*, m.p. 233—234°, the optically active forms of (II) giving an inactive product. Oxidation ($KMnO_4$) of (II) gives $COPh\cdot C_{10}H_7$-1 and reduction

(HI–P) affords *αγ-diphenyl-αγ-di-*1-*naphthyl-Δ^α-propene*, m.p. 167—169°, which is obtained when the reaction product of β-phenyl-β-1-naphthylpropiophenone and 1-$C_{10}H_7$·MgBr is dehydrated with Ac_2O. The mechanism of the asymmetric catalysis is discussed. F. R. S.

Diphenylindenes. III. Hydrogenation of diphenylindenes and diphenylindone and other reactions of this group. A García Banús and E. de Salas (Anal. Fís. Quím., 1935, **33**, 53—71).—Reduction of both 1 : 2- and 2 : 3-diphenylindene (I) (cf. A., 1929, 688) by P and HI or Na and amyl alcohol gives two forms of diphenylhydrindene (cf. Bergmann *et al.*, A., 1930, 1030), whilst catalytic H (PtO_2) yields solely the isomeride, m.p. 124—125°. Contrary to de Fazi (A., 1931, 731), the existence of two forms of (I) is considered not to be due to stereoisomerism. Reduction of 2 : 3-diphenylindone (II) with Zn and AcOH or H_2 and Pt or PtO_2 with HCl gives cis-2 : 3-*diphenylhydrindone* (III), m.p. 157—158°, and 1-*hydroxy*-2 : 3-*diphenylindene* (IV), two forms, m.p. 84—85° and 134—135°, both of which give the same Ac derivative (cf. Thiele *et al.*, A., 1912, i, 866), whilst Fe and AcOH or H_2 and Pt on $BaSO_4$ or PtO_2 yields *trans*-2 : 3-diphenylhydrindone (V), m.p. 100—101° (cf. Schenk *et al.*, A., 1928, 1035). (III) is converted into (V) by distillation at 22 mm., whilst they both give the same *phenylhydrazone*, m.p. 137—139°, and a sparingly sol. polymeride, m.p. 200—201° (decomp.), which by distillation under reduced pressure yields (V), which is also formed from $CHPh_2$·CHPh·COCl with $AlCl_3$ in CS_2. (III) is assigned the *cis*-structure on the basis of its greater reactivity than (V) and its formation by hydrogenation in acid. (III), (IV), and (V) with PbO_2 all yield (II). 1-Amino-2 : 3-diphenylindene hydrochloride (improved prep.) (A., 1929, 688) with $HgCl_2$ and NaOH in EtOH gives 1-*imino*-2 : 3-*diphenylindene*, m.p. 141—142°. Similarly 9-aminofluorene yields 9-*iminofluorene*, m.p. 123—124°, which with dil. HCl gives fluorenone. F. R. G.

Naphthalene homologues of coal tar. O. Kruber and W. Schade [in part with W. Morneweg] (Ber., 1936, **69**, [*B*], 1722—1729).—A neutral fraction, b.p. 258—260°, is converted by conc. H_2SO_4 at 45° into 1 : 7-*dimethylnaphthalene*-4-*sulphonic acid* [*Na* salt (I); corresponding *sulphonamide*, m.p. 204—205°], transformed by superheated steam in presence of 70% H_2SO_4 into 1 : 7-*dimethylnaphthalene* (II), b.p. 261—262°/760 mm. (*picrate*, m.p. 121°). (I) is transformed by molten KOH into 1 : 7-*dimethyl*-4-*naphthol*, m.p. 102°, which with PhN_2Cl gives the *dye* $C_{18}H_{16}ON_2$, m.p. 137°. (II) is oxidised by CrO_3 in 50% AcOH to 1 : 7-*dimethyl*-5 : 8-*naphthaquinone*, m.p. 135—136°, and 3-methyl-*o*-phthalic acid, m.p. 157°. Treatment of (II) with dil. HNO_3 followed by $K_3Fe(CN)_6$ gives 1 : 7-$C_{10}H_6(CO_2H)_2$, m.p. 308° (decomp.) after softening (*Me*$_2$ ester, m.p. 89°), which is obtained synthetically by converting 2 : 8-NH_2·$C_{10}H_6$·SO_3H into 2 : 8-CN·$C_{10}H_6$·SO_3H and thence into 2 : 8-*dicyanonaphthalene*, m.p. 152—154°, which is hydrolysed with 40% KOH–EtOH. The isolation of 2-$C_{10}H_7$Et from a suitable coal-tar fraction is described. H. W.

Nitration of 2-ethylnaphthalene. Synthesis of 2-ethyl-8-naphthol. G. Levy (Compt. rend., 1936, **203**, 337—339).—Nitration of 2-$C_{10}H_7$Et affords 2 : 1-$C_{10}H_6$Et·NO_2 and an oil which is reduced by Fe and AcOH to a mixture of amines from which 2 : 8-$C_{10}H_6$Et·NH_2 [*hydrochloride*; *Ac* derivative (I), m.p. 148·5—149° (corr.)] is separated. (I) is converted by 1% H_2SO_4 at 200° into 2-*ethyl*-8-*naphthol* (II) m.p. 51° (*picrate*, m.p. 145°), synthesised as follows. $(CH_2·CO)_2O$, PhEt, and $AlCl_3$ in benzine afford β-*p*-ethylbenzoylpropionic acid, m.p. 102—103°, reduced (Clemmensen) to γ-*p*-ethylphenylbutyric acid, m.p. 70°, the *chloride*, b.p. 143—145°/18 mm., of which is cyclised by $AlCl_3$ to 8-*keto*-2-*ethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b.p. 152—154°/18 mm. [*semicarbazone*, m.p. 197° (corr.)], dehydrogenated by Se to (II). H. W.

1- and 2-Mononitroanthracene. M. Battegay and P. Bœhler (Compt. rend., 1936, **203**, 333—335).—Treatment of 2-anthracenyldiazonium borofluoride (I) in 80% H_2SO_4 with conc. HNO_3 at 10—15° and of the solution with EtOH at 70° affords N_2, MeCHO, a violet-black insol. substance, and 1-*nitroanthracene*, m.p. 146°, identified by reduction to 1-aminoanthracene and oxidation to 1-nitroanthraquinone. (I) is transformed by $NaNO_2$ in presence of $CuSO_3$–Cu_2SO_3 into anthracene and 2-*nitroanthracene*, m.p. 172°, identified by conversion into 2-aminoanthracene and 2-nitroanthraquinone. H. W.

Extremely weak acids.—See this vol., 1069.

Dissociable organic oxides. 9-Phenylanthracene and its derivatives. C. Dufraisse, L. Velluz, and (Mme.) L. Velluz (Compt. rend., 1936, **203**, 327—329).—9-Phenylanthracene (I), 10-bromo- (II) and 10-*iodo*- (III), m.p. 132°, -9-phenylanthracene, 9-*phenylanthracene*-10-*carboxylic acid* (IV), m.p. 264°, and its *Me* ester (V), m.p. 162° (obtainable only by use of CH_2N_2), are photo-oxidisable, but the process is complicated by the evolution of halogen from (II) and (III) and is irregular in the case of (IV). (I) gives an *oxide*, $C_{20}H_{14}O_2$, in poor yield by reason of its extreme sensitiveness to light, and its thermal decomp. occurs vigorously at about 155° with appreciable liberation of O_2. (V) affords a normally dissociable *oxide*, $C_{22}H_{16}O_4$. The presence of *meso*-H is invariably an obstacle to the dissociability of the photo-oxides of anthracene. H. W.

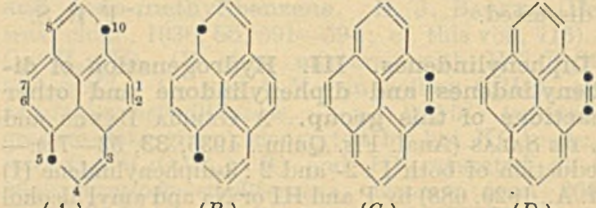
Hydrophenanthrenes and related ring systems from dieneinenes. P. S. Pinkney, G. A. Nesty, R. H. Wiley, and C. S. Marvel (J. Amer. Chem. Soc. 1936, **58**, 972—976; cf. A., 1933, 591, 1270).—1-*Acetylenyl*cyclo*hexanol* (I), b.p. 83—84°/25 mm., m.p. 31—32° (*Hg* derivative, m.p. 175·5—176·5°), obtained in 81% yield from *cyclo*hexanone (II) (in Et_2O–*tert.*-amyl alcoholic K *tert.*-amyloxide) and Et_2O–C_2H_2 at —15° followed by aq. NH_4Cl, is converted by successive treatment with MgEtBr and *cyclo*pentanone or (II) into α-1-*hydroxy*cyclo*pentyl*-β-1-*hydroxy*cyclo*hexylacetylene* (III), m.p. 93—94°, or αβ-di-1-hydroxy*cyclo*hexylacetylene (IV) [also obtained by Dupont's method (A., 1914; i, 134)], respectively. (IV) is dehydrated (40% H_2SO_4) to αβ-*di*-Δ^1-cyclo*hexenylacetylene*, b.p. 126—128°/3 mm., which is reduced [H_2 (1500—2000 lb.), Raney Ni, methyl*cyclo*hexane, 250°] to *s*-di*cyclo*hexylethane, b.p. 93—94°/2 mm., and is converted by AcOH–conc. H_2SO_4 or, better, 85% HCO_2H into 9-*keto-Δ^{11}-dodecahydrophenanthrene* (V), b.p. 130—132°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 227—228°), and a little of an isomeric *ketone*, m.p. 93—94° (2 : 4-*dinitrophenylhydrazone*, m.p. 186—187°) [not identical with the 9-keto-Δ^{10}-dodecahydrophenanthrene, m.p. 88·5—90° (2 : 4-*dinitrophenylhydrazone*, m.p. 226—227°), of Rapson and Robinson (A., 1935, 1498)]. (IV) and AcOH–conc. H_2SO_4 give a smaller yield of (V) and a little dodecahydrobenzil (? 2 : 4-*dinitrophenylhydrazone*, m.p. 120—121°), whilst (IV) and 85% HCO_2H afford (V) and 3-keto-2 : 5-di*cyclo*pentamethylenetetrahydrofuran (2 : 4-*dinitrophenylhydrazone*, m.p. 162—162·5°) (Dupont, *loc. cit.*). Clemmensen reduction of (V) gives Δ^{11}-*dodecahydrophenanthrene*, b.p. 81—82°/1·5 mm. (cf. Schmidt and Mezger, A., 1907, i, 1022), which is reduced further (Ni; as above) to *tetradecahydrophenanthrene*, b.p. 86—89°/2 mm. (also obtained by similar repeated reduction of phenanthrene); this could not be dehydrogenated (Se at 300—320°).

(III) is similarly dehydrated to α-Δ^1-cyclo*pentenyl*-β-Δ^1-cyclo*hexenylacetylene*, b.p. 103—104°/2·5 mm., reduced (Ni) to α-cyclo*pentyl*-β-cyclo*hexylethane*, b.p. 74—76°/2 mm., and cyclised (as above) to 4-*keto*-1 : 2-*trimethylene*-3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*octahydronaphthalene*, b.p. 114—116°/2·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 221—222°) (ozonolysis product, adipic acid), which is reduced (Clemmensen) to the 1 : 2-*trimethyleneoctahydro*-, b.p. 74—76°/3 mm., and thence (Ni) to the 1 : 2-*trimethylenedecahydro-naphthalene*, b.p. 71—72°/2·5 mm. H. B.

cis- and trans-as-Octahydrophenanthrene. J. van de Kamp and E. Mosettig (J. Amer. Chem. Soc., 1936, 58, 1062—1063).—Repeated fractionation of *as*-octahydrophenanthrene (from 1-β-phenylethyl*cyclo*hexanol and P_2O_5) gives 70% of *cis-* (I), b.p. 142·6—142·8°/9·2 mm., and 20% of *trans-* (II), b.p. 135·5—135·7°/10·5—10·8 mm., forms. (I) gives an Ac derivative, an oil (semicarbazone, m.p. 211—213°), oxidised to an octahydrophenanthrenecarboxylic acid, m.p. 230—232°; the corresponding derivatives from (II) have m.p. 94—94·5°, 230—231·5°, and 226—228°, respectively. H. B.

Spiran by-product in the phenanthrene synthesis. M. T. Bogert (Science, 1936, 84, 44–45; cf. A., 1933, 601).—Evidence that the lower-b.p. fraction obtained from the crude *as*-octahydrophenanthrene by van de Kamp and Mosettig (preceding abstract) is a spiran and not a phenanthrene derivative is summarised. L. S. T.

Aromatic hydrocarbons. XXI. Structure of pyrene according to the anellation process. E. Clar (Ber., 1936, 69, [*B*], 1671—1685).—Chemical evidence permits the following fine structures for pyrene. The absorption spectrum of it and its derivatives indicates *A* (*symm-pyr*-condition) and not *B*; it reacts at positions 3 and 8 and, with *K*=6, is the first representative of the *symm-pyr*-condition of which there is no sign in Ph_2 or phenanthrene. The state *B* can be forced by anellation in the 3 : 4 : 9 : 10-position. The absorption spectra of pyrenes invariably give evidence of the *o*-condition represented by *C* or *D*, of which the former is preferred by reason of its derivation from phenanthrene.



(*A.*) (*B.*) (*C.*) (*D.*)

In addition, in certain derivatives a further *o*-condition is evidenced apparently related to the unsymmetrical structure of the mol. Greater complexity of the mol. has no spectroscopically novel effect. Pyrene, *o*-$C_6H_4Me{\cdot}COCl$, and $AlCl_3$ in C_6H_6 yield 3-*o*-*toluoylpyrene*, m.p. 139—140·5° or m.p. 107° and m.p. 137° after re-solidification, whence 2′ : 3′-naphtha-3 : 4-pyrene (I), m.p. 265—266°, and a *substance*, $C_{24}H_{14}$, m.p. (indef.) 220—260° (very unstable *picrate*, m.p. 205°). 3-Pyrenoyl-*o*-benzoic acid, m.p. 220—222°, passes at >300° into 3 : 4-phthaloylpyrene, m.p. 250—251°. (I) and maleic anhydride in boiling xylene afford 2′ : 3′-*naphtha*-3 : 4-*pyrene*-endo-1′ : 4′-αβ-*succinic anhydride*, decomp. 298—300°, or m.p. 272—273° and decomp. 298—300° after re-solidification. CPh_2Cl_2, pyrene, and $AlCl_3$ in C_6H_6 yield 1′-*phenylindeno*-2′ : 3′ : 3 : 4-*pyrene*, m.p. 279—280°. 3 : 5 : 8-*Tribromopyrene* has m.p. 259—260°. H. W.

Perylene and its derivatives. XLVIII. The perylene tribromide of K. Brass and E. Clar. A. Zinke and A. Pongratz (Ber., 1936, 69, [*B*], 1591—1593).—Repetition of the work of Brass and Clar (A., 1932, 57) shows that it is impossible to obtain a stable product of const. composition by the addition of Br to perylene (I) in C_6H_6; the intermediate substance is very unstable and the Br content varies with conditions of prep. and age. (I) exposed in a thin layer to Br vapour rapidly absorbs 4 Br but evolution of HBr commences immediately. Recrystallisation of the product from boiling PhMe or $PhNO_2$ leads to 3 : 9-dibromoperylene. The intermediate substance is therefore $C_{20}H_{12}Br_4$ and, probably, a normal tetrabromide. H. W.

Preparation of rubrene. W. Koblitz and H. Wittmeyer (Ber., 1936, 69, [*B*], 1806).—Triphenylpropargyl alcohol is gradually treated with $SOCl_2$ containing a little $AlCl_3$ at 0°; the solution is washed with H_2O and aq. $NaHCO_3$ and the C_6H_6 solution is evaporated to dryness. The residue is heated at 120°/vac., thereby giving rubrene in 40% yield. H. W.

Attempted partial synthesis of ergostane. E. Fernholz (Ber., 1936, 69, [*B*], 1792—1795).—Norcholyl Me ketone, m.p. 112° [*semicarbazone*, m.p. 235° (decomp.)], obtained by heating a mixture of Ba cholanate (I) and $Ba(OAc)_2$ at 400°, is converted by treatment with $MgPr^{\beta}Br$ followed by boiling AcOH into Δ^{24}-ψ-ergostene, $C_{19}H_{31}{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CMe_2$, m.p. 103°, hydrogenated (Pt-sponge in Et_2O) to ψ-*ergostane*, m.p.

64°, $[\alpha]_D^{19}$ +25·3° in $CHCl_3$. (I) and $(EtCO_2)_2Ba$ at 370°/vac. afford very small amounts of norcholyl Et ketone [*semicarbazone*, m.p. 215° (decomp.)]. Ba *allo*cholanate yields *nor*allo*cholyl Me ketone*, m.p. 113° [*semicarbazone*, m.p. 218° (decomp.)], whence two *hydrocarbons*, $C_{28}H_{48}$, m.p. 128°, $[\alpha]_D$ +19·4° in $CHCl_3$, and m.p. 54—56°, $[\alpha]_D$ +21·6° in $CHCl_3$, each of which is hydrogenated to ergostane, m.p. 81—82°, $[\alpha]_D^{18}$ +22·9°, probably containing an isomeride in small amount. H. W.

Preparation of aniline from benzene and ammonia in a high-frequency high-tension field. V. K. Razumov (Men. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 261—268).—The reactions $C_6H_6 + NH_3 + O \rightarrow NH_2Ph + H_2O$; $C_6H_6 + NH_2Ph + O \rightarrow NHPh_2 + H_2O$; $C_6H_6 + O \rightarrow PhOH$ take place when the gas mixture is passed through a high-frequency high-tension electromagnetic field. R. T.

Alkylation of aniline in presence of mixed catalysts. III. Mono-methyl- and -ethyl-aniline. N. I. Schujkin, A. N. Bitkova, and A. F. Ermilina (J. Gen. Chem. Russ., 1936, 6, 774—779).—The velocity of alkylation of NH_2Ph by EtOH or MeOH in presence of Al_2O_3 is > with Al_2O_3–Fe_2O_3, but the product in the latter case is free from dialkyl derivatives. NHPhMe is obtained in 45% yield in presence of 1 : 1 Al_2O_3–Fe_2O_3 at 350°, and NHPhEt in 59% yield at 350° (Al_2O_3 30—40, Fe_2O_3 60—70%). The latter reaction is more rapid than the former, but loss of alcohol due to side reactions is greater. R. T.

Hexaiodotellurates of aromatic amines etc.—See this vol., 1079.

Addition of chlorocarbamide to doubly-bound carbon. I. Ribas, E. Tapia, and A. Caño (Anal. Fís. Quím., 1936, 34, 501—506).—*cyclo*Hexene with $NH_2·CO·NHCl$ (I) gives, in addition to the chlorohydrin (cf. Detoeuf, A., 1922, i, 236), 2-*chloro*cyclo*hexylcarbamide*, m.p. 185°, which with aq. KOH yields 2-amino-4 : 5-*cyclo*hexano-oxazoline (cf. Birckenbach *et al.*, A., 1931, 832). (I) with CHPh:CHMe gives probably β-*chloro*-β-*phenyl*iso*propylcarbamide*, m.p. 135°, and a liquid, b.p. 110—113°, probably a mixture of CHPhCl·CHMeCl with the chlorohydrin. F. R. G.

Phenylurethane anæsthetics. II. E. S. Cook and T. H. Rider (J. Amer. Chem. Soc., 1936, 58, 1079—1081; cf. A., 1930, 1031).—γ-*Dimethylamino*-, m.p. 131—132·5° (all m.p. are corr.), γ-*diethylamino*-, m.p. 140·5—142·5°, γ-*di*-n-*propylamino*-, m.p. 159·5—160·5°, γ-di-*n*-butylamino-, m.p. 123—124°, γ-(β′-*phenylethylmethylamino*)-, m.p. 192·5—193·5°, and γ-*piperidino*-, m.p. 169—169·5°, -*propyl*, and β-*diethylamino*-, m.p. 137·5—138·5°, and β-*piperidino*-, m.p. 88—89·5°, -α-*methylethyl phenylcarbamate hydrochlorides* are prepared from the appropriate amino-alcohol and PhNCO in Et_2O followed by HCl. $NHPh·CO_2·CH_2·CH_2·NEt_2$,HCl has m.p. 142·5—143·5° (lit. 138—139°). Pharmacological data are given; the $NHPh·CO_2·$ group appears to be more active than p-$NH_2·C_6H_4·CO_2·$ in causing anæsthesia of mucous surfaces. γ-(β′-*Phenylethylmethylamino*)*propyl alcohol*, b.p. 155—157°/12 mm., is prepared from $CH_2Ph·CH_2·NHMe$ and $CH_2Br·CH_2·CH_2·OH$. H. B.

Molecular rearrangement of sulphenanilides. III. M. L. Moore and T. B. Johnson (J. Amer. Chem. Soc., 1936, 58, 1091—1094; cf. A., 1935, 1120, 1359; this vol., 200).—2 : 4-$NO_2·C_6H_3Cl·SCl$ and NH_2Ar in Et_2O give 4-*chloro*-2-*nitrobenzenesulphen-anilide* (I), m.p. 102°, and -o-*toluidide* (II), m.p. 127°, whilst $NO_2·C_6H_4·SCl$ and o-$C_6H_4Cl·NH_2$ afford o- (III), m.p. 130°, and p- (IV), m.p. 99—101°, -*nitrobenzenesulphen*-o-*chloroanilide*. (I) heated alone at 150—160° or, better, in an excess of NH_2Ph at 180—190° rearranges to 4-*chloro*-2-*nitro*-4′-*amino-diphenyl sulphide*, m.p. 127—129°; similarly, (II) in o-$C_6H_4Me·NH_2$ gives 4-*chloro*-2-*nitro*-4′-*amino*-3′-*methyldiphenyl sulphide*, m.p. 113—115°, whilst (IV) in o-$C_6H_4Cl·NH_2$ affords 3′-*chloro*-4-*nitro*-4′-*aminodiphenyl sulphide*, m.p. 127—129°. o-$NO_2·C_6H_4·S·NH·C_6H_4R$ (R=H, *o*-Cl, *o*- and *p*-Me) heated with $C_6H_4R'·NH_2$ (R′=H, *o*- and *p*-Me) give the aminodiphenyl sulphides derived from o-$NO_2·C_6H_4·S·NH·C_6H_4R'$; such displacement does not occur when R′ is *o*-Cl. Thus, (III) heated in *o*- and p-$C_6H_4Me·NH_2$ affords 2-nitro-4′-amino-3′, m.p. 101—103°, and 2-nitro-2′-amino-5′-, m.p. 105—107°, -methyldiphenyl sulphide, respectively. All ArS·NHAr′ are decomposed by acids to Ar_2S_2 and NH_2Ar'. H. B.

Preparation of naphthidine. S. Cohen and R. E. Oesper (Ind. Eng. Chem. [Anal.], 1936, 8, 306—307).—α-$C_{10}H_7·NH_2$,HCl is diazotised and converted with Na_2SO_3 into azonaphthalene (yield quant.), which is then reduced in EtOH at the boil with $SnCl_2$ and HCl. The solution is rapidly cooled, and more HCl added to ppt. naphthidine hydrochloride. The crude base obtained on basification is recryst. from EtOH–C_5H_5N. The yield is 33·5%, m.p. 198—199°. S. C.

Derivatives of (A) *NN*-2 : 4-di- [and] (B) *NN*-2 : 4 : 6-tri-nitrophenylmethylhydrazine. J. J. Blanksma and (Miss) M. L. Wackers (Rec. trav. chim., 1936, 55, 655—660, 661—668).—$NHMe·NH_2$ and 2 : 4-$C_6H_3Cl(NO_2)_2$ (I) or 2 : 4 : 6-$C_6H_2Cl(NO_2)_3$ in warm EtOH give NN-2 : 4-*di*-, m.p. 144° (*Ac* derivative), and NN-2 : 4 : 6-*tri-nitrophenylmethylhydrazine*, m.p. 171° (*Ac* derivative, m.p. 222°) [structure proved by condensation with aldehydes and expected because (I) condenses much faster with NH_2Me than with NH_3]. Aldehydes are readily characterised by these hydrazines; reaction is rapid in hot EtOH containing a little H_2SO_4 and the m.p. are conveniently lower than those of the non-methylated compounds. The following are described: 2 : 4-*di*- and 2 : 4 : 6-*tri-nitrophenylmethylhydrazones* and 2 : 4 : 6-*trinitrophenylhydrazones*, respectively, of PhCHO, m.p. 206°, 214°, 270°, *o*-, m.p. 176°, 164°, 246°, *m*-, m.p. 195°, 159°, 252°, and p-$C_6H_4Cl·CHO$, m.p. 199°, 211°, 255°, *o*- (II), m.p. 183°, 224°, 265° (lit. 215°), *m*-, m.p. 239°, 216°, 251°, and p-$NO_2·C_6H_4·CHO$, m.p. 246°, 233°, 250°, *o*-, m.p. 191°, 220°, 275°, and p-$OH·C_6H_4·CHO$ (III), m.p. 225°, 224°, 284°, p-$OMe·C_6H_4·CHO$, m.p. 185°, 180°, 252°, 3 : 4-CH_2O_2:$C_6H_3·CHO$, m.p. 212°, 236°, 260°, 4 : 3-$OH·C_6H_3(OMe)·CHO$ (IV), m.p. 178°, 200°, 276°, furfuraldehyde, m.p. 190°, 204°, 246° (lit. 230°), hydroxymethyl- (V), m.p. 100°, 196°,

216°, and 5-methyl-furfuraldehyde, m.p. 171°, 182°, 218°, MeCHO, m.p. 118°, 152°, —; 2 : 4-*dinitrophenylhydrazones* of *o*-, m.p. 209°, *m*-, m.p. 256°, and *p*-$C_6H_4Cl\cdot CHO$, m.p. 270°, (II), m.p. 252°, (III), $+H_2O$, m.p. 260°, (IV), m.p. 270°, and (V), m.p. 184°.
R. S. C.

p-tert.-Butylphenol, a substance with the odour of Russian leather. G. Sandulescu and S. Sabetay (Riechstoffind., 1935, 10, 84; Chem. Zentr., 1935, ii, 3021).—*p-tert*.-Butylphenol, m.p. 93—94°, b.p. 233—234°/762 mm., 127·5—128·5°/20 mm., and its Et, b.p. 110—111°/13 mm., Pr^{α}, b.p. 122—123°/13 mm., Pr^{β}, b.p. 113—114°/13 mm., Bu^{α}, b.p. 136—137°/13 mm., and Bu^{β}, b.p. 126—128°/13 mm., *ethers* are described. H. N. R.

Sulphonation of 2-ethylnaphthalene. Synthesis of 6-ethyl-β-naphthol. G. Lévy (Compt. rend., 1936, 202, 1679—1680; cf. A., 1932, 734, 842; 1933, 1287).—2-$C_{10}H_7Et$ with conc. H_2SO_4 at 95° affords 2 : 6-$C_{10}H_6Et\cdot SO_3H$, the Na salt of which after fusion with alkali gives 6-*ethyl*-β-*naphthol* (I), m.p. 97—98° (*picrate*, m.p. 106—107°). *p*-Methoxybenzyl chloride with $CHNa(CO_2Et)_2$ affords *Et_2* p-*methoxybenzylethylmalonate*, b.p. 161°/2 mm.; the corresponding *acid*, m.p. 131·5—132·5°, is decarboxylated to α-p-*methoxybenzylbutyric acid*, b.p. 195°/13 mm., the *amyl* ester, b.p. 188°/13 mm., of which is reduced by Bouveault's method to β-p-*methoxybenzyl*-n-*butyl alcohol* (II), b.p. 165°/13 mm. (II) with $SOCl_2$ and some $NPhMe_2$ affords the *chloride*, b.p. 160°/13 mm., which cannot be converted directly into β-p-*methoxybenzylvaleronitrile* (III), b.p. 172—175°/13 mm., but only through the *I*-compound, b.p. 165°/13 mm. (III) with boiling MeOH–KOH affords β-p-*methoxybenzylvaleric acid*, b.p. 205°/13 mm., the *chloride*, b.p. 175°/13 mm., of which with $AlCl_3$ in hexane is cyclised to 6-*methoxy*-4-*keto*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 180°/13 mm. (*semicarbazone*, m.p. 171—172°), which is reduced (Clemmensen) to 6-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 148—153°/13 mm. Dehydrogenation followed by demethylation yields 6-*methoxy*-2-*ethylnaphthalene*, m.p. 57—59°, and (I), respectively.
J. L. D.

Dyes from resorcinol, sulphuric acid, and alcohols. E. Bertonasco (G. Farm. Chim. Sci. affini, 1935, 84, 58—64; Chem. Zentr., 1935, ii, 3096).—MeOH, EtOH, PrOH, $Bu^{\beta}OH$, and glycerol all give dyes on warming with resorcinol and conc. H_2SO_4. The products may be esters of resorcinoldisulphonic acid. H. N. R.

Exchange between dihydroxybenzenes and heavy water. F. K. Münzberg (Z. physikal. Chem., 1936, B, 33, 39—46).—In the exchange of H for D between resorcinol (I) and D_2O in which it is dissolved the H of OH groups are exchanged immeasurably rapidly, two H of the nucleus in the *o*-position to OH are exchanged at a measurable rate by way of an enol–keto transformation (cf. following abstract), and the other two nuclear H are replaced directly and very slowly. Orcinol (II) behaves similarly. In quinol (III) H of both OH are rapidly exchanged, but all the nuclear H are exchanged very slowly and at the same rate; apparently there is no kinetically effective enol–keto change. It is inferred that in the ring of (I) and (II) the C–C linkings are alternately double and single and do not exchange positions periodically, whilst in the ring of (III) there are at most two double linkings. R. C.

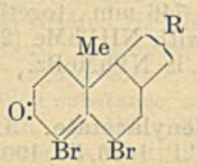
Exchange between trihydroxybenzenes and heavy water. F. K. Münzberg (Z. physikal. Chem., 1936, B, 33, 23—38).—In the exchange of H for D between pyrogallol (I) and D_2O in which it is dissolved the H of OH groups are exchanged immeasurably rapidly, and the nuclear H more slowly, but each at a different rate. Experiments with Na gallate (II) show that in (I) the two nuclear H in the *o*-position to OH are exchanged more rapidly than the isolated nuclear H. All the H of phloroglucinol are quickly exchanged. Since in C_6H_6 the H is not readily exchanged for D (A., 1934, 1080), it is inferred that H attached to C is readily exchanged if keto–enol tautomerism is possible. Hence the above compounds must contain double linkings, as, *e.g.*, in the Kekulé formula. It appears that in the ring in (I) and (II) two different kinds of C–C linking alternate with each other and exchange positions on the average once in $1\cdot4\times10^6$ sec. at 50°.
R. C.

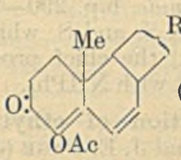
Lichen substances. LXVIII. Preparation of higher homologues of orcinol. Y. Asahina [with M. Miyasaka and T. Sekizawa] (Ber., 1936, 69, [*B*], 1643—1646).—Et α-3 : 4 : 5-trimethoxybenzoylpropionate is converted by 5% KOH–EtOH at 60° into 3 : 4 : 5-trimethoxypropiophenone, m.p. 53°, reduced by Na and EtOH to 3 : 5-dimethoxypropylbenzene, b.p. 147°/29 mm., converted by boiling HI (*d* 1·7) into divarin, b.p. 169°/8 mm. (monohydrate, m.p. 51°; Br_3-derivative, m.p. 99°). Similarly Et α-3 : 4 : 5-trimethoxybenzoylvalerate yields 3 : 4 : 5-trimethoxyvalerophenone, converted successively into olivetol Me_2 ether and olivetol (Br_3-derivative, m.p. 87°). *Et* α-3 : 4 : 5-*trimethoxybenzoyl*-n-*heptoate*, m.p. 39°, is transformed into 3 : 4 : 5-*trimethoxyphenyl*-n-*hexyl ketone*, b.p. 175—176°/4 mm., m.p. 29° (*semicarbazone*, m.p. 112°), whence *sphaerophorol Me_2 ether*, b.p. 150°/5 mm., and sphaerophorol, b.p. 175—176°/5 mm. (monohydrate, m.p. 57°; Br_3-derivative, m.p. 75°). H. W.

Catalytic hydrogenation of some epoxides. P. Weill and F. Kayser (Bull. Soc. chim., 1936, [v], 3, 841—844).—Catalytic reduction (Ni) of triphenylethylene oxide in EtOH at 35—45° yields solely αββ-triphenylethyl alcohol. Similarly α-anisyl-ββ-diphenyl- and α-tolyl-β-phenyl-ethylene oxides give solely α-anisyl-ββ-diphenyl- and α-tolyl-β-phenylethyl alcohol. H. G. M.

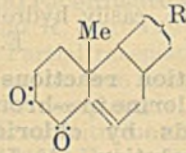
Transformations of brominated derivatives of cholesterol. II. H. H. Inhoffen (Ber., 1936, 69, [*B*], 1702—1710).—A modified prep. of the tribromoketone (I) from cholesterol is given (cf. this vol., 854). Treatment of (I) with KOAc in C_6H_6–EtOH affords the *dibromide* (II), m.p. 162—163° (decomp.), the constitution of which is supported by its absorption spectrum. When boiled with EtOH containing a little HBr it gives the enol ether of cholestene-3 : 6-dione. Further treatment of (I) with

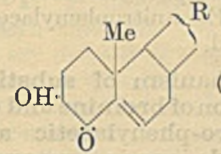
KOAc in EtOH gives the *enol acetate* (III), m.p. 158—159° after softening, also obtained directly from


(II.)


(III.)

(I). Hydrolysis of (III) by HCl–EtOH leads to the *o-diketone* (IV or V), m.p. 160—161°, which reduces

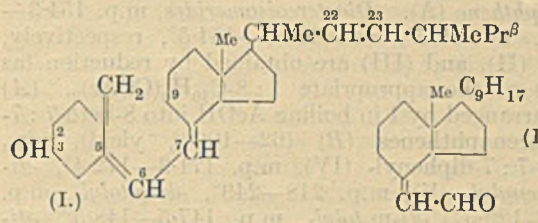

(IV.)


(V.)

NH_3–Ag_2O and gives a red-brown colour with $FeCl_3$; its absorption spectrum indicates the presence of three conjugated double linkings. It yields a *dioxime*, decomp. about 180° after softening, and a *quinoxaline* derivative, $C_{33}H_{46}N_2$, m.p. 175° (decomp.), which is unchanged by boiling Ac_2O. In support of structure (V) it reacts with Ac_2O without regenerating (III) and contains 1 OH (Zerevitinov). H. W.

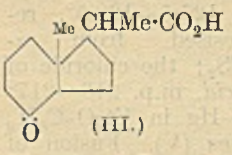
***allo*Cholesterol and *epiallo*cholesterol.** R. Schoenheimer and E. A. Evans, jun. (J. Biol. Chem., 1936, **114**, 567—582).—Cholestenone and hot $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give a 1 : 1 mol. *compound*, m.p. 141°, $[\alpha]_D^{21}$ +84·1° in C_6H_6, separable by digitonin (I) into allo*cholesterol* (II), m.p. 132°, $[\alpha]_D^{23}$ +43·7° in C_6H_6 [pptd. by (I); *acetate*, m.p. 85°], and epiallo*cholesterol* (III), m.p. 84°, $[\alpha]_D^{24}$ +120·8° in C_6H_6 [not pptd. by (I); *acetate*, m.p. 82·5°]. Hydrogenation (PtO_2) of (II) in amyl ether gives *epi*coprosterol (IV), that of (III) gives (IV) and *epi*dihydrocholesterol. (II) or (III) with hot 0·033*N*-HCl–EtOH gives $\Delta^{2:4}$-*cholestadiene* (V), m.p. 79°, $[\alpha]_D^{23}$ −112·5° in C_6H_6 (absorption max. at 229, 235, and 240 mμ). The substance hitherto known as (II) is a 2 : 3 mixture of (II) and cholesterol (VI), since (*a*) its behaviour is paralleled by that of a synthetic mixture and (*b*) with HCl it gives about 40% of (V) with unchanged (VI), the latter being hitherto considered as the product of the reaction. Thirty-one examples show that the Rosenheim test is given only by those sterols having conjugated ethylenic linkings or capable of giving this system [*e.g.*, containing CH:CH·C(OH):CH] under the conditions of the test, but that compounds with CO·C:C·C:C do not give it. The hydrocarbon, $C_{26}H_{42}$, of Windaus *et al.* (A., 1915, i, 677) gives the test. The usual *cis–trans* nomenclature (referring to the H on $C_{(5)}$) of sterols may be misleading and offers difficulty with Δ^4- and Δ^5-compounds. It is proposed to name compounds according to the relation of the Me on $C_{(10)}$ to, first, the OH on $C_{(3)}$ and, second, the H on $C_{(5)}$. Thus, dihydro-, *epi*dihydro-, *allo*-, and *epiallo*-cholesterol are *cis-trans*, *trans-trans*, *cis*, and *trans*, respectively, coprosterol and *epi*coprosterol are *cis-cis* and *trans-cis*, cholesterol and *epi*cholesterol are *cis* and *trans*, respectively. Only those compounds with a *cis*-configuration of OH–Me (first title) are pptd. by (I), and relationships are always clear. R. S. C.

Sterol group. XXIV. Constitution of calciferol. I. M. Heilbron, R. N. Jones, K. M. Samant, and F. S. Spring. **XXV. Reactions of the isomeric ethers of cholesterol.** J. H. Beynon, I. M. Heilbron, and F. S. Spring (J.C.S., 1936, 905—907, 907—910; cf. this vol., 981).—XXIV. Calciferol is (I), because (*a*) with CrO_3–AcOH or $KMnO_4$, best at room temp., it gives an *aldehyde* (II), $C_{21}H_{34}O$,



(I.) (II.)

an oil, the *semicarbazone*, m.p. 242°, of which has an absorption spectrum very similar to that of citral-semicarbazone (proof of the 7 : 8 ethylenic linking) and (*b*) with O_3 gives CH_2O (proof of the presence of CH_2:) and a *keto-acid* (III), $C_{13}H_{12}O_3$ (*semicarbazone*, m.p. 219°) (proof of the 22 : 23 and 7 : 8 ethylenic linkings).



(III.)

XXV. Cholesteryl *p*-toluenesulphonate (IV) and KOAc in hot EtOH give cis-*cholesteryl Et ether* (V), m.p. 47°, $[\alpha]_D^{20}$ +49·78° in $CHCl_3$, and in $CH_2Ph·OH$ at 100° some *trans*- and much cis-*cholesteryl benzyl ether* (VI), b.p. 170°/0·001 mm., $[\alpha]_D^{20}$+15·77° in $CHCl_3$. (V), (VI), and the *cis*-Me ether with halogen acids in AcOH give the cholesteryl halide and with Br–AcOH–Et_2O give 3 : 5 : 6-tribromocholestane. *Cholesteryl iodide*, thus prepared, has m.p. 106·5—107°, $[\alpha]_D^{20}$ −11·94°. The *trans*-ethers do not eliminate the alkoxy-group thus; with Br there are formed the *dibromides*, m.p. 107°, 80°, and 107°, $[\alpha]_D^{20}$ −52·95°, −50·75°, and −50·2° in $CHCl_3$, of *trans*-cholesteryl Me, Et, and CH_2Ph ether, respectively. Thus, the *cis*-ethers may have a Δ^4-ethylenic linking, but this is unlikely as they do not give the colour with $SbCl_3$ given by *allo*cholesterol and its Me ether and ψ-cholestene. (IV) with aq. KOH or aq. KOAc gives cholesterol and dicholesteryl ether (VII), with KOAc–AcOH gives *trans*-cholesteryl acetate, with Ag_2O–H_2O or dil. H_2SO_4 gives (VII), and with H_2SO_4–EtOH *trans*-cholesteryl Et ether. The *cis–trans* nomenclature requires confirmation. R. S. C.

Derivative of vitamin-*D* and several sterols. M. Sumi (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 635—640).—The following have been prepared: *calciferyl*, m.p. 132°, $[\alpha]_D^{20}$ +149·97°, *cholesteryl*, m.p. 168°, $[\alpha]_D^{20}$ 0°, *sitosteryl*, m.p. 190°, $[\alpha]_D^{20}$ +2·5°, and *ergosteryl* β-*naphthoate*, m.p. 175°, and the *anthraquinone-2-carboxylates* of the last three, m.p. 170° (or >250°), $[\alpha]_D^{20}$ 0°, m.p. 189° (or 253°), $[\alpha]_D^{20}$ −1·3°, and m.p. 195° (or 200°), respectively. W. O. K.

Pinacol–pinacolin rearrangement. VIII. Rearrangement of 7 : 8-dihydroxy-7 : 8-diarylacenaphthenes. W. E. Bachmann and E. J. H. Chu (J. Amer. Chem. Soc., 1936, 58, 1118—1121).—The following are prepared from acenaphthenequinone and MgArBr in Et_2O–C_6H_6: 7 : 8-dihydroxy-7 : 8-

diphenyl-, m.p. 154·3—155·3° [a stereoisomeride, m.p. 173·5—175·6° (lit. 171—173°), is obtained from 1 : 8-$C_{10}H_6Bz_2$ and 1%Na–Hg in Et_2O–C_6H_6 followed by dil. AcOH], -*di*-p-*diphenylyl*-, m.p. 220°, -*di*-p-*tolyl*- (I), m.p. 182—182·5°, *di*-m-*tolyl*-, m.p. 152·3—153·3°, -*dianisyl*-, m.p. 168—169°, -*diphenetyl*-, m.p. 144·5—145·5°, -*di*-p-*chlorophenyl*- (II), m.p. 222—223°, and -*di*-p-*fluorophenyl*- (III), m.p. 220—221°, -*acenaphthene* (A). *Diastereoisomerides*, m.p. 154·3—155·3°, 78—79·5°, and 153·5—154·5°, respectively, of (I), (II), and (III) are obtained by reduction (as above) of the appropriate 1 : 8-$C_{10}H_6(COAr)_2$. (*A*) are rearranged by I in boiling AcOH into 8-keto-7 : 7-diarylacenaphthenes (*B*) (62—100% yield), viz., 8-keto-7 : 7-diphenyl- (IV), m.p. 171·3—172·4°, -*di*-p-*diphenylyl*- (V), m.p. 248—249°, -*di*-p-*tolyl*-, m.p. 128·5—129·5°, -*di*-m-*tolyl*-, m.p. 147·5—148·5°, -*dianisyl*-, m.p. 151·5—152·5°, -*diphenetyl*-, m.p. 122·8—123°, -*di*-p-*chlorophenyl*-, m.p. 145·5°, and -*di*-p-*fluorophenyl-acenaphthene*, m.p. 127·5—128·5°, respectively. (IV) is synthesised from α-$C_{10}H_7\cdot CPh_2\cdot COCl$ and $SnCl_4$ in CS_2; the chloride of *di*-p-*diphenylyl-α-naphthylacetic acid*, m.p. 216—217° (from the CAr_3Cl and 45% Na–Hg in Et_2O–C_6H_6 followed by CO_2), similarly gives (V). Fusion of (*B*) with KOH at (usually) 250° affords 8-benzhydryl-, m.p. 226°, 8-*di*-p-*diphenylylmethyl*-, m.p. 247—248°, 8-*di*-p-, m.p. 159·3—160·3°, and -m-, m.p. 189·5—190·5°, -*tolylmethyl*-, 8-*dianisylmethyl*-, m.p. 173·5—174·5°, 8-*diphenetylmethyl*-, m.p. 170—171°, 8-*di*-p-*chlorophenylmethyl*-, m.p. 225—226°, and 8-*di*-p-*fluorophenylmethyl*-, m.p. 221—222°, -1-*naphthoic acid*, whilst oxidation (CrO_3, AcOH) of (*A*) gives 1: 8-$C_{10}H_6Bz_2$ and 1 : 8-*di*-p-*phenylbenzoyl*-, m.p. 219—220°, 1 : 8-*di*-p-, m.p. 181·5—182·5°, and -m-, m.p. 157·3—158·3°, -*toluoyl*-, 1 : 8-*dianisoyl*-, m.p. 215—216°, 1 : 8-*diethoxybenzoyl*-, m.p. 197—197·5°, 1 : 8-*di*-p-*chlorobenzoyl*-, m.p. 188°, and 1 : 8-*di*-p-*fluorobenzoyl*-, m.p. 166·5—167·5°, -*naphthalene*. The appropriate (*A*) with dry HCl in cold $CHCl_3$ afford the dichlorides, converted by NaI in $COMe_2$ into 7 : 8-diphenyl-, m.p. 161·3°, 7 : 8-*di*-p-*diphenylyl*-, m.p. 189·5—190·5°, 7 : 8-*di*-p-*tolyl*-, m.p. 137·2—137·7°, 7 : 8-*di*-p-*chlorophenyl*-, m.p. 204·5—205·5° (obtained using AcOH–HI), and 7 : 8-*di*-p-*fluorophenyl*-, m.p. 153·5—154·5°, -*acenaphthylene*. H. B.

Conversion of carboxylic acids into their homologues. F. ARNDT and B. EISTERT (Ber., 1936, **69**, [*B*], 1805).—Mainly a reply to Preobrashenski *et al.* (A., 1935, 872; this vol., 1002) concerning the transitions, $R\cdot CO_2H \rightarrow R\cdot COCl \rightarrow R\cdot CO\cdot CHN_2 \rightarrow CH_2R\cdot CO_2H$. The yields of esters from diazoketones (I) are considerably improved if Ag_2O is added in successive small quantities to the mixtures of (I) and alcohols. Ag_2O acts as alkali and source of colloidal Ag which is the actual catalyst. H. W.

Synthesis of dibenzoyl disulphide. R. S. SHELTON and T. H. RIDER (J. Amer. Chem. Soc., 1936, **58**, 1282—1284).—Bz_2S_2, m.p. (tube) 129—130° (decomp.), (bar) 132°, is prepared by oxidation (H_2O_2) of BzSH (from BzCl and 35% aq. NaHS in O_2). H. B.

Action of secondary amines on dibenzoyl disulphide. L. SZPERL and M. WASILEWSKA (Rocz. Chem., 1936, **16**, 207—212).—$(Ph\cdot CO\cdot S\cdot)_2$ (I) and $NHPr^{a}_2$ in C_6H_6 at room temp. yield *benzdi*-n-*propylamide*, b.p. 290—291°/746 mm., together with BzSH, H_2S, and S, whilst with NHPhMe (27 hr. at the b.p.) the chief product is NPhMeBz. (I) does not react with $NHPh_2$. R. T.

Nitration of ethyl phenylacetate. J. F. J. DIPPY and J. E. PAGE (J.S.C.I., 1936, **55**, 190—192T).—Nitration of $CH_2Ph\cdot CO_2Et$ with (*a*) HNO_3–H_2SO_4 gives 2 : 4-dinitrophenylacetic acid, (*b*) HNO_3–AcOH, Et *p*-nitrophenylacetate (poor yield), and (*c*) HNO_3–Ac_2O, Et *o*-nitrophenylacetate, easily hydrolysed to the acid. F. R. S.

Mechanism of substitution reactions. Substitution of bromine and chlorine in α-bromo- and α-chloro-phenylacetic acids by chloride and bromide ions in aqueous solution. M. J. YOUNG and A. R. OLSON (J. Amer. Chem. Soc., 1936, **58**, 1157—1162).—The heats of activation and collision factors for these reactions are determined at 15—50° and compared with those for the halogenosuccinate system (A., 1934, 847; this vol., 569). In accordance with theory, the reaction *l*-$CHBrPh\cdot CO_2H + Cl^- \rightarrow$ *d*-$CHClPh\cdot CO_2H + Br^-$ is accompanied by complete inversion in configuration. H. B.

Configuration of aminophenylacetic acid. H. REIHLEN and L. KNÖPFLE (Annalen, 1936, **523**, 199—210).—*Me* d(—)-*α-aminophenylacetate* (*hydrochloride*, m.p. 202°, $[\alpha]_D$ −121° in H_2O; *Ac*, m.p. 114—117°, $[M]_{5893}$ −363° in MeOH, and *Bz* derivative, m.p. 101·5°, $[M]_{5893}$ −270° in MeOH; $[M]$ are given also for 3 other λ and 6 solvents) readily affords d(—)-*α-aminophenylacetamide*, decomp. > 150°, $[M]^{20}_{3893}$ −188° in H_2O (*Ac*, m.p. 175°, $[\alpha]_D$ −242° in $CHCl_3$, and *Bz* derivative, m.p. 217·5°, $[\alpha]_D$ −119° in $CHCl_3$), stable to dehydrating agents. Hydrogenation (Pt–C) of *d*(—)-α-$NH_2\cdot CHPh\cdot CO_2H$ (I) in 2*N*-HCl at 70° gives d(—)-*α-amino*cyclo*hexylacetic acid* (II) {*Me* [*hydrochloride*, m.p. 186° (decomp.); *Ac*, m.p. 118°, $[M]_D$ −53° in $CHCl_3$, and *Bz* derivative, m.p. 130°, $[M]_D$ −105° in $CHCl_3$] and *Et* ester (*hydrochloride*, m.p. 167°; *Ac*, m.p. 93°, $[M]_D$ −116° in $CHCl_3$, and *Bz* derivative, m.p. 125°, $[M]_D$ −117° in $CHCl_3$)}. Comparison of $[M]$ in 4 solvents of the *Ac*, m.p. 61·5°, $[M]_D$ +112° in $CHCl_3$, and *Bz* derivative, m.p. 110·5°, $[M]_D$ +115° in $CHCl_3$, of the Me ester and the *Bz* derivative, m.p. 77·5—78°, $[M]_D$ +137° in $CHCl_3$, of the Et ester of *l*(+)-valine (III) and of the effects of acid and alkali on [α] for (III) with the corresponding $[M]$ and changes in the (II) series proves the configurations of (I) and (II) stated above. *dl*-(I) is hydrogenated only after purification by way of the nitrate. R. S. C.

Condensation of (A) dihydroxydiethylamine with potassium cyanide, formaldehyde, and benzaldehyde, (B) β-hydroxypropylamine with potassium cyanide, benzaldehyde, and *cyclo*hexanone. V. F. LIUBOMUDROV (Ukrain. Chem. J., 1936, **11**, 119—122, 123—126).—(A) $NH(CH_2\cdot CH_2\cdot OH)_2$,HCl, aq. KCN, and aq. CH_2O (12 hr. at room temp.) afford $CN\cdot CH_2\cdot N(CH_2\cdot CH_2\cdot OH)_2$, hydrolysed by aq. HCl to yield di-(β-hydroxyethyl)-aminoacetic acid. *Di-(β-hydroxyethyl)aminophenyl-*

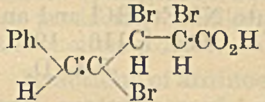
acetic acid, m.p. 143—144°, is prepared analogously, using PhCHO in place of CH_2O.

(B) $OH\cdot CHMe\cdot CH_2\cdot NH_2$,HCl, PhCHO, and aq. KCN afford β-*hydroxypropylaminophenylacetonitrile*, m.p. 90° (*hydrochloride*, m.p. 121—122°), yielding an unidentified substance, m.p. 199—200°, when hydrolysed with aq. HCl. The product obtained when *cyclo*hexanone is substituted for PhCHO in the reaction is 1-*cyano*-1-β-*hydroxypropylamino*cyclo*hexane*, m.p. 49—50° (*hydrochloride*, m.p. 115°). R. T.

Partial racemisation. I. H. Lettré, H. Barnbeck, and H. Staunau (Ber., 1936, **69**, [*B*], 1594—1598).—Partial racemates are defined as compounds related to the true racemates or pseudoracemates in which the components differ either sterically or by different substitution. Investigation of the system $OH\cdot CHPh\cdot CO_2H$–hexahydromandelic acid shows that *r*-mandelic acid (I) is a true racemate. *r*-Hexahydromandelic acid (II) is also racemic. l(+)-Mandelic acid and d(−)-hexahydromandelic acid give a partial racemate the m.p. of which is > that of either component. (I) and (II) give an unbroken series of mixed crystals. Where partial racemism occurs [(I)–(II); malic acid (III)–tartaric acid (IV)] the corresponding racemic compounds are isomorphous, and where this is not the case [(I)–(III); (I)–(IV)] the racemic compounds are not isomorphous. Further examples are quoted from the lit. and the relationship may be general. H. W.

β-Arylacrylic compounds. Y. de Schuttenbach (Ann. Chim., 1936, [xi], **6**, 53—96).—Comparison of the rates of hydrolysis of $CHPh\colon CPh\cdot CO_2Me$ (I), *p*-$OMe\cdot C_6H_4\cdot CH\colon CPh\cdot CO_2Me$ (II), and $CH_2O_2\colon C_6H_3\cdot CH\colon CPh\cdot CO_2Me$ (III) and of esterification of the corresponding acids shows that the appreciable retarding action of the double linking is accentuated when β-Ph is replaced by β-$CH_2O_2\colon C_6H_3$ and further enhanced by β-*p*-$C_6H_4\cdot OMe$. The absorption in the ultra-violet is displaced towards the visible during passage from (I) to (II) and thence to (III). *Me* α-*phenyl*-β-p-*anisylacrylate*, b.p. 250°/25 mm., m.p. 90—91°, and *Me* α-*phenyl*-β-*piperonylacrylate*, m.p. 106—107°, are obtained by condensation of $CH_2Ph\cdot CO_2Me$ with Na powder and the appropriate aldehyde. $CPhMe\colon CH\cdot CO_2Me$ is transformed by MgMeI into the alcohol, $CPhMe\colon CH\cdot CMe_2\cdot OH$, dehydrated to β-*phenyl*-γ-*methyl*-Δ^{β}-*butene*, b.p. 107—108°/18 mm., which is oxidised to COPhMe by CrO_3 in AcOH. $CPhMe\colon CH\cdot CO_2Me$ and MgPhBr give $CPh_2Me\cdot CH_2\cdot COPh$. Addition of $CHPh\colon CPh\cdot CN$ to $CH_2Ph\cdot MgCl$ in boiling Et_2O gives αβγ-*triphenylbutyronitrile*, m.p. 192°; under apparently identical conditions a second experiment gave the impure *diastereoisomeride*, m.p. 129—131°, hydrolysed to *acids*, $C_{22}H_{20}O_2$, m.p. 138° and m.p. 152—153°, respectively. H. W.

αβγ-Tribromocinnamylacetic [-tribromo-δ-phenyl-Δ^{γ}-pentenoic] acid. H. Lohaus and W. Gussmann (Annalen, 1936, **523**, 294—299).—αβγ-Tribromo-δ-phenyl-Δ^{γ}-pentenoic acid (I), m.p. 157°, obtained from αβ-*trans*-γδ-*cis*-γ-*cis*-bromo-δ-phenylpentadienoic acid (II) and Br–$CHCl_3$, gives (II) with NaI–$COMe_2$ or Zn dust in dry Et_2O, and with $KMnO_4$–$COMe_2$ gives an *isomeride*, $+2H_2O$, m.p. 163°, and *meso*dibromotartaric acid, whence it follows that (I) has the annexed formula.



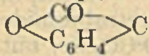
(I) gives a 2 : 1 pyridinium *compound*, $C_{27}H_{23}O_4NBr_6$, decomp. 142°, stable to hot AcOH, converted into its components by hot alcoholic alkali or conc. HCl. The mother-liquor from the prep. of (I) yields the 1 : 1 pyridinium *compound*, m.p. 85°, of a dibromophenyl-Δ^{γ}-pentenoic acid. The Me ester of (II) with Br–$CHCl_3$ gives the *Me* ester, m.p. 59—60°, of (I) [also obtained from (I) by CH_2N_2], and a *Me dibromo*-δ-*phenyl*-Δ^{γ}-*pentenoate* (III), m.p. 117°, isolated in this reaction as 1 : 1 pyridinium *compound* (IV), m.p. 151° (decomp.), or by the action of C_5H_5N–Et_2O on the tetrabromide of (II). (IV) and O_3 in H_2O give $CHO\cdot CO_2Me$, but no PhCHO, wherefore it is probable that one Br in (III) is in the Ph nucleus. R. S. C.

5 : 6 : 7 : 8-Tetrahydro-α-naphthylamine-4-carboxylic acid, and certain of its derivatives. S. I. Sergievskaja and V. V. Nesvadba (J. Gen. Chem. Russ., 1936, **6**, 633—666).—4-Nitro-5 : 6 : 7 : 8-tetrahydro-1-naphthylamine is diazotised, and the product is treated with CuCN to yield the corresponding 1-*nitrile* (I), m.p. 121°, reduced by $SnCl_2$ in HCl at room temp. to 4-*cyano*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthylamine*, m.p. 114° (*Ac* derivative, m.p. 203°). (I) and HCl (140° : 10 hr.) yield 1-*nitro*-5 : 6 : 7 : 8-*tetrahydronaphthalene*-4-*carboxylic acid*, m.p. 161—162°, the *Et* ester, m.p. 37°, of which is reduced by H_2 (Pt-black) to the *Et* ester, m.p. 90° (*Ac* derivative, m.p. 165—166°), of 5 : 6 : 7 : 8-tetrahydro-α-naphthylamine-4-carboxylic acid, from which the free *acid*, m.p. 188° (decomp.), is obtained by boiling with EtOH–KOH. R. T.

New type of vanadyl salicylate. P. Brauman (Compt. rend., 1936, **202**, 1992—1994).—Addition of Li_2CO_3 to a mixture of 50% aq. $VOCl_2$ and excess of $OH\cdot C_6H_4\cdot CO_2Et$ in MeOH gives a mixture of a blue product [of type $R'O(VO)O\cdot C_6H_4\cdot CO_2R$] and a green product, which cannot be separated. With Bu or *iso*amyl *p*-hydroxybenzoate only the green *compounds* are formed, of composition $V_2C_{15}H_{28}O_{10}$ and $V_2C_{16}H_{30}O_{10}$, respectively. With the Ph ester the green *product* is $V_2C_{12}H_{22}O_{10}$, and is a derivative of $OH\cdot C_6H_4CO_2Me$. The green compounds probably contain MeOH of crystallisation. The composition $OMe(VO)O(VO)O\cdot C_6H_4\cdot CO_2R,3MeOH$ is suggested. H. J. E.

Action of mixed organo-magnesium compounds on aromatic *N*-diethylamides with phenolic groups. P. Couturier (Compt. rend., 1936, **202**, 1994—1996; cf. A., 1926, 837; 1927, 458).—*Diethylamides* (m.p. in parentheses), prepared by interaction of the acid chloride and $NHEt_2$, of the following acids are described: *o*- (104°), *m*- (84°), and *p*-hydroxybenzoic (121°), protocatechuic [(149—151°) Ac_2 derivative (72°)], gallic [(137°) Ac_3 derivative (113°)], and anisic acid (42°). Salicyldiethylamide with MgEtBr in boiling Et_2O, C_6H_6, or Bu_2O affords *o*-*hydroxypropiophenone*, m.p. 20—22°. The *m*- and *p*-analogues react less easily. The other amides do not react. *p*-$OMe\cdot C_6H_4\cdot CO\cdot NEt_2$ reacts more readily with MgEtBr than the phenol to give *p*-$OMe{\cdot}C_6H_4{\cdot}COEt$ and a *tert*. base, the hydrochloride of which decomposes at 90° into $NHEt_2,HCl$ and an unsaturated hydrocarbon (cf. A., 1905, i, 116; 1926, 942; 1910, i, 728). J. L. D.

Oxidation of phenols with peracetic acid. C. Grundmann [with H. Trischmann] (Ber., 1936, **69**, [*B*], 1755—1757).—*o*-Hydroxycinnamic acid is oxidised by AcO_2H in the dark to *cis-cis*-muconic acid in very small amount; in presence of light a more or less complete isomerisation to the *trans-trans*-acid takes place. 2 : 2′-Dihydroxydiphenyl gives 2′-*hydroxy*-2-*phenyl*-p-*benzoquinone*, m.p. 193° (Berl; corr.; decomp.), and α-o-*hydroxyphenylmuconolactone*,

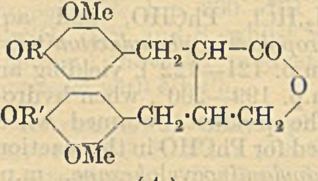


$O<\substack{CO-\\C_6H_4}>C{:}CH{\cdot}CH{:}CH{\cdot}CO_2H$, m.p. 194—195° (Berl; corr.). H. W.

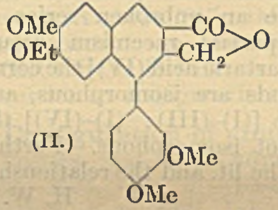
Action of light on β-bromobenzylidenepyruvic acid. M. Reimer (J. Amer. Chem. Soc., 1936, **58**, 1108—1111).—Exposure of a saturated C_6H_6-solution of $CHPh{:}CBr{\cdot}CO{\cdot}CO_2H$ (I) (A., 1924, i, 642) in a quartz tube and N_2 atm. to bright sunlight gives about 80% of a *dimeride* (II) (+2MeOH), m.p. 201° (decomp.) [*Me_2* ester (CH_2N_2), m.p. 212° and then slow decomp.]; a yellow intermediate is formed in diffused light (not in dark); this changes rapidly in sunlight into (II). In presence of dry O_2, (II) and ββ(or βγ)-*dibromo*-γ(or β)-*hydroxy*-α-*keto*-γ-*phenylbutyric acid* (+H_2O), m.p. 107° (opaque; clear at 109°) [also obtained from (I) and Br (vapour) in H_2O], are produced. In moist C_6H_6, some ββγ-*trihydroxy*-α-*keto*-γ-*phenylbutyric acid* (III), m.p. 134° (decomp.), is formed. Finely-divided (I) is converted by prolonged exposure into a *dimeride*, m.p. 285° (decomp.) (*Me_2* ester, m.p. 233—234°). (III), which is cleaved by alkaline H_2O_2 to mandelic acid and $H_2C_2O_4$ and is oxidised by $Pb(OAc)_4$ to PhCHO, is also formed from (I) and $KMnO_4$ in aq. $COMe_2$+ little H_2SO_4 at −3° to 0°. H. B.

Hydrogen esters of tetrachlorophthalic acid. V. Teterin and S. Zonis (J. Gen. Chem. Russ., 1936, **6**, 658—662).—*Mono-esters* of the following alcohols are obtained by boiling with $C_6Cl_4(CO_2H)_2$ (I) in C_6H_6, C_6H_6–$CHCl_3$, or C_6H_6–Et_2O (2—10 hr.): MeOH, m.p. 142°; *n*-, m.p. 105—106°, *iso*-, m.p. 97—98°, and *sec*.-BuOH, m.p. 121—122°; *iso*-$C_5H_{11}{\cdot}OH$, m.p. 112—113°; β-naphthylethyl alcohol, m.p. 179—180°; *p*-nitrobenzyl alcohol, m.p. 179—180°; *cyclo*hexanol, m.p. 150—151°; menthol, m.p. 99—100°; benzhydrol, m.p. 149—150°; β-naphthylmethyl-, m.p. 155—155·5°, and -ethyl-carbinol, m.p. 159·6—161°. Esters were not obtained under the above conditions with $OH{\cdot}CH_2{\cdot}CH_2Cl$, $OH{\cdot}CHCl{\cdot}CHCl{\cdot}CH_2Cl$, PhOH, and certain *tert*. alcohols. The esters of alcohols of low b.p. decompose when heated to yield the anhydride of (I) and the alcohol, whilst esters of *sec*. alcohols afford (I) and unsaturated hydrocarbons. R. T.

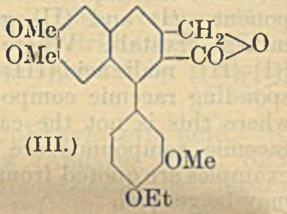
Constituents of natural phenolic resins. VII. Arctigenin. R. D. Haworth and W. Kelly (J.C.S., 1936, 998—1003; cf. this vol., 985).—*l*-Arctigenin is *A* (R=H, R′=Me), (*a*) because its *Et ether* (I) (*A*, R=Et, R′=Me; obtained by hot Et_2SO_4–KOH–EtOH), an oil [*Br_2*-, m.p. 128—129°, and (*NO_2*)$_2$-derivative, m.p. 166—167°], has an absorption spectrum identical with that of the dl-*ether*, which is synthesised, whereas the isomeric ether (*A*; R=Me, R′=Et; also synthesised) has an absorption spectrum which, although similar, has a lower intensity of absorption at the max., 2800 A., and (*b*) because (I) with $Pb(OAc)_4$–AcOH at 80° gives the *lactones* (II), m.p. 223—224°, of 6-*methoxy*-7-*ethoxy*-1-3′ : 4′-*dimethoxyphenyl*-2-*hydroxymethylnaphthalene*-3-*carboxylic acid*, and (III), m.p. 247—248°, of 6 : 7-*dimethoxy*-1-3′-*methoxy*-4′-*ethoxyphenyl*-3-*hydroxymethylenenaphthalene*-2-*carboxylic acid*, which are both synthesised. The lactones, also synthesised, expected from the alternative formula (*A*; R=Me, R′=Et) for (I) differ from (II) and (III). 3 : 4-$OMe{\cdot}C_6H_3(OEt){\cdot}CHO$ (IV) and hot $KMnO_4$–aq. $NaHCO_3$ give 3-methoxy-4-ethoxybenzoic acid, m.p. 195°, the chloride (V), b.p. 158—160°/0·2 mm., m.p. 73°, of which with NaOEt and $CH_2Ac{\cdot}CO_2Et$ gives a product, converted by NH_4Cl–aq. NH_3 into *Et* 3-*methoxy*-4-*ethoxybenzoylacetate*, m.p. 79—78°. With NaOEt and $CH_2Br{\cdot}CO_2Et$ this yields β-3-*methoxy*-4-*ethoxybenzoylpropionic acid* (VI), m.p. 136—137°. *O*-Ethyleugenol and I–HgO–Et_2O–H_2O give the *oxide* (VII), b.p. 137—138°/0·2 mm., m.p. 37—38°. (IV), $CN{\cdot}CH_2{\cdot}CO_2Na$, and aq. NaOH give α-*cyano*-β-3-*methoxy*-4-*ethoxyphenylacrylic acid*, m.p. 212—213°, reduced (2% Na–Hg–CO_2; 0°) to α-*cyano*-β-3-*methoxy*-4-*ethoxyphenylpropionic acid*, m.p. 152—153° [*Me* ester (VIII), m.p. 61—62°]. The Na derivative of (VIII) with *O*-methyleugenol oxide in EtOH gives β-3 : 4-*dimethoxybenzyl*-α-3-*methoxy*-4-*ethoxybenzylbutyrolactone* [=*dl*-(I)], m.p. 105—106° [*Br_2*-, m.p. 88—89°, and (*NO_2*)$_2$-derivative, m.p. 159°]. 3 : 4-$(OMe)_2C_6H_3{\cdot}CH_2{\cdot}CNa(CN){\cdot}CO_2Me$ and (VII) in EtOH give α-3 : 4-*dimethoxybenzyl*-β-3-*methoxy*-4-*ethoxybenzylbutyrolactone* (*A*; R=Me, R′=Et), m.p. 95—96° [*Br_2*-, m.p. 99—100°, and (*NO_2*)$_2$-derivative, m.p. 172—173°]. (VII) and $CHNaAc{\cdot}CO_2Et$ in EtOH at room temp. afford α-*acetyl*-β-3-*methoxy*-4-*ethoxybenzylbutyrolactone*, m.p. 87—88°, the Na derivative of which with 3 : 4-$(OMe)_2C_6H_3{\cdot}COCl$ in C_6H_6 yields α-3 : 4-*dimethoxybenzoyl*-β-3-*methoxy*-4-*ethoxybenzylbutyrolactone*, m.p. 129—130°, converted by warming with HCl–MeOH and subsequent dehydration with $KHSO_4$ at 180° into the *lactone*, m.p. 189—190°, of 6-*methoxy*-7-*ethoxy*-1-3′:4′-*dimethoxyphenyl*-3-*hydroxymethyl*-3:4-*dihydronaphthalene*-2-*carboxylic acid*, which is oxidised by $Pb(OAc)_4$ to the *lactone*, m.p. 243—244°, of 6-*methoxy*-7-*ethoxy*-1-3′ : 4′-*dimethoxyphenyl*-3-*hydroxy*-



(A.)



(II.)



(III.)

methylnaphthalene-2-carboxylic acid. α-Acetyl-β-3 : 4-dimethoxybenzylbutyrolactone and (V) lead similarly to α-3-*methoxy*-4-*ethoxybenzoyl*-β-3 : 4-*dimethoxybenzylbutyrolactone*, m.p. 123—124°, the *lactone*, m.p. 192—193°, of 6 : 7-*dimethoxy*-1-3′-*methoxy*-4′-*ethoxyphenyl*-3-*hydroxymethyl*-3 : 4-*dihydronaphthalene*-2-*carboxylic acid*, and (III). 3:4-$(OMe)_2C_6H_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2Na$ (IV), and Ac_2O at 100° give the *γ-lactone*, m.p. 180°, converted by hot NaOMe into β-3 : 4-*dimethoxybenzoyl*-α-3-*methoxy*-4-*ethoxybenzylidenepropionic acid*, m.p. 188—189°; when the β-*methylene*-derivative (prep. by CH_2O and aq. NaOH at room temp.), m.p. 180°, thereof is kept with HCl–AcOH and the product is heated first with dil. NaOH and then with dil. acid, (II) is obtained. (VI), veratraldehyde, and Ac_2O lead similarly to β-3-*methoxy*-4-*ethoxybenzoyl*-α-3 : 4-*dimethoxybenzylidenepropionic acid* (IX), m.p. 189—190°, by way of the *γ-lactone*, m.p. 162—163°, and thence to the β-*methylene*-derivative, m.p. 176—177°, of (IX), and the *lactone*, m.p. 214—215°, of 6 : 7-*dimethoxy*-1-3′-*methoxy*-4′-*ethoxyphenyl*-2-*hydroxymethylnaphthalene*-3-*carboxylic acid.* R. S. C.

Bile acids. XLIX. Oxidation product of bilianic acid. Effect of carbamide on oxidations with nitric acid. M. SCHENCK (Z. physiol. Chem., 1936, **242**, 81—88; cf. this vol., 605).—Oxidation of bilianic acid (I) at room temp. with HNO_3 gives the tetrabasic *acid* (II), $C_{21}H_{35}O_{10}N$, decomp. 175—180°. There is no action if $CO(NH_2)_2$ is added. Hot HNO_3 oxidises (I), but only small yields of biloidanic acid are obtained. $CO(NH_2)_2$ does not interfere with the action of cold HNO_3 on the hydroxamic acid $C_{21}H_{36}O_8N_2$, but it prevents the oxidation of the lactam of bilianic acid oxime. W. McC.

Aldehydes and hydroxyaldehydes of the polymethylenic series. I. Transformations of hexahydrobenzaldehyde. E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1936, **6**, 697—703).—Hexahydrobenzaldehyde (I) and $HgBr_2$ in C_5H_5N (140—144°; 4 hr.) yield *cyclo*pentyl Me ketone, higher yields of which are obtained from (I), H_2SO_4, and $HgSO_4$ in aq. EtOH. R. T.

Transformations between stereoisomeric aldoximes. W. THIELACKER and L. H. CHOU (Annalen, 1936, **523**, 143—153).—β-2 : 6-Dichloro-3-nitrobenzaldoxime is quantitatively converted by cold, dil. NaOH into HCl and 6-chloro-3-nitrosalicylonitrile, whereas the α-isomeride (II) is completely unchanged. The proportion of (I) in a mixture of the oximes can therefore be determined by titration (Volhard). It is thus shown that the same equilibrium mixture is formed from (I) or (II) under the action of very conc. HCl. When the method is applied to the equilibration of (I) and (II) in org. media it is found that the end-point of the titration is greatly obscured by the solvent, and the results are not very accurate. In EtOH, $COMe_2$, and EtOAc (I) tends to an equilibrium greatly displaced towards (II); (II) is isomerised much more slowly, and accidental catalytic influences are strongly in evidence. Attempts to follow the isomerisation of (I) and (II) in Et_2 *d*-tartrate by alteration of [α] are hampered by the great dependence of this val. on time, but experiments with α- and β-anisaldoxime in the same solvent show that an equilibrium and not a complete isomerisation occurs (position of equilibrium deduced from m.p. of products). Similarly, an equilibrium ensues in the molten oximes. H. W.

Reactions of aminoethyl alcohol with aldehydes and malonic acid. A. I. KIPRIANOV and T. S. KUSNER (J. Gen. Chem. Russ., 1936, **6**, 641—644).—$NH_2\cdot CH_2\cdot CH_2\cdot OH$ (I), $CH_2(CO_2H)_2$, and PhCHO in EtOH at the b.p. yield cinnamic acid; in the cold the *product*, m.p. 135—136° (decomp.), is $CHPh{:}C(CO_2H)_2,NH_2\cdot CH_2\cdot CH_2\cdot OH$ (II). An analogous *product*, m.p. 137° (decomp.), is obtained when furfuraldehyde is taken in place of PhCHO, whilst salicylaldehyde gives the *salt*, m.p. 196—197°, of (I) and coumarin-3-carboxylic acid, and piperonaldehyde yields an unstable product, converted into piperonylideneacrylic acid during recrystallisation. (II) yields cinnamic acid when heated at the m.p., and $CHPh{:}C(CO_2H)_2$ when treated with aq. acids. R. T.

Conversion of aldoximes into carboxylic acids by hot alkali. Elimination of water from aldoximes. E. JORDAN and C. R. HAUSER (J. Amer. Chem. Soc., 1936, **58**, 1304—1305).—Some aromatic β-aldoximes (I) are converted (slowly) into a mixture of the α-oxime (II) and the corresponding acid by 2*N*-NaOH at 97—100°; (II) undergo slower conversion into the acid. (I) thus eliminates H_2O [to give ArCN which is then hydrolysed] more readily than (II). Benzaldoxime and *m*-nitro-, *p*-methoxy-, and 3 : 4-methylenedioxy-benzaldoximes are used. In agreement with Brady and Goldstein (A., 1927, 973), α- and β-furfuraldoximes similarly undergo interconversion; furoic acid is produced in greater amount from the β. H. B.

Synthesis of a pyrogallolaldehyde [methyl ether]. F. MAUTHNER (J. pr. Chem., 1936, [ii], **145**, 313—317).—CPh_2Cl_2 (prep. in excellent yield by PCl_5 at 160—170°), b.p. 167°/14 mm., and Me gallate in C_6H_6 give *Me* 3-*hydroxy*-4 : 5-*diphenylmethylenedioxybenzoate*, which with MeI–NaOMe yields *Me* 4 : 5-*diphenylmethylenedioxy*-3-*methoxybenzoate*, hydrolysed by fuming HCl to *gallic acid* 3-*Me ether*, m.p. 220—222°, which at 250—270° gives pure pyrogallol 1-Me ether, b.p. 136—137°/13 mm., m.p. 37—40°. With $Zn(CN)_2$ (modified prep.) and HCl in Et_2O this affords 3 : 4-*dihydroxy*-2-*methoxybenzaldehyde* (less probably the 2 : 3-*dihydroxy*-4-*methoxy*-compound), m.p. 118—119° [green $FeCl_3$ colour; p-*nitrophenylhydrazone*, m.p. 249—250° (decomp.)], which with MeI–K_2CO_3–$COMe_2$ yields 2 : 3 : 4-$(OMe)_3C_6H_4\cdot CHO$ (p-*nitrophenylhydrazone*, m.p. 198—199°). R. S. C.

Reaction of αβ-dibromo-β-phenylethyl methyl ketone with azides. V. A. KUZMIN and S. G. FRIDMAN (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, **2**, 55—67).—$CHPhBr\cdot CHBr\cdot COMe$ does not react with NaN_3 in Et_2O, C_6H_6, or ligroin, at the b.p., or with AgN_3 in Et_2O; in boiling EtOH or $COMe_2$ a *monoazide*, $C_{10}H_9ON_3$, m.p. 78—79° [*semicarbazone*, m.p. 167° (decomp.)], is obtained. R. T.

Ketones of the formula CHRPh·CO·R′. P. JULLIEN (Bull. Soc. chim., 1936, **3**, [v], 1347—1353;

cf. A., 1930, 213).—MgPr$^\beta$Br with CHPrPh·CN in PhMe or xylene at 80—100° affords *α-phenyl-*n*-butyl Pr$^\beta$ ketone*, b.p. 134—135°/17 mm. (*semicarbazone*, m.p. 152°). The following are prepared similarly: *α-phenyl-β-methyl-*n*-propyl Et ketone*, b.p. 130—145°/23 mm. (*semicarbazone*, m.p. 181°); *α-phenyl-*n*-amyl Pr$^\beta$*, b.p. 142—145°/15 mm. (*semicarbazone*, m.p. 107°), and *Bu$^\beta$ ketone*, b.p. 280—282° (*semicarbazone*, m.p. 116°); *α-phenyl-γ-methyl-*n*-butyl Me*, b.p. 138—145°/22 mm. (*semicarbazone*, m.p. 118°), *Et*, b.p. 132—140°/14 mm. (*semicarbazone*, m.p. 127—128°), *Pr$^\beta$*, b.p. 139—144°/19 mm. (*semicarbazone*, m.p. 156°), and *Bu$^\gamma$ ketone*, b.p. 153—160°/20 mm. (*semicarbazone*, m.p. 109°). MgPrBr with α-phenyl-β-methylbutyramide in Et_2O affords *α-phenyl-β-methyl-*n*-propyl Pr ketone*, b.p. 135—137°/23 mm. (*semicarbazone*, m.p. 162°). J. L. D.

Preparation of dibenzyl and benzyl methyl ketones. C. D. Hurd and C. L. Thomas (J. Amer. Chem. Soc., 1936, **58**, 1240; cf. A., 1933, 821).—$CH_2Ph{\cdot}CO_2H$ heated with Ac_2O–KOAc followed by slow distillation gives 41% of $CO(CH_2Ph)_2$ (I) and 16% of $COMe{\cdot}CH_2Ph$ (II). (I) and (II) arise by pyrolysis of $(CH_2Ph{\cdot}CO)_2O$ and $CH_2Ph{\cdot}CO_2Ac$, respectively. H. B.

Condensation of *o*-nitrobenzaldehyde with *m*-nitroacetophenone. Photochemical behaviour of the resulting *o*-nitro-derivatives. I. Tanasescu and E. Tanasescu (Bull. Soc. chim., 1936, [v], **3**, 865—870).—$o\text{-}NO_2{\cdot}C_6H_4{\cdot}CHO$, $m\text{-}NO_2{\cdot}C_6H_4{\cdot}COMe$, and NaOEt–EtOH–$Et_2O$ yield 2 : 3′-dinitrochalkone (I), m.p. 163° (lit. 161°), and *m-nitrophenyl β-hydroxy-β-o-nitrophenylethyl ketone* (II), m.p. 124° (*Bz derivative*, m.p. 142°), converted quantitatively by EtOH–alkalis into indigotin. (I) is not formed when the Et_2O in the foregoing mixture is replaced by EtOH. (I) when boiled with NaOH–EtOH and then treated with HCl gives indigotin. Reduction of (I) and (II) with Zn–AcOH gives unidentified *products*, m.p. 159° and m.p. 178°, respectively. (II) when irradiated loses 1 mol. of H_2O, giving a *substance*, m.p. about 300°, with acidic properties. H. G. M.

Anthracene structure of dissociable organic oxides. Properties of anthracene photo-oxide. C. Dufraisse and M. Gérard (Compt. rend., 1936, **202**, 1859—1861).—Anthracene photo-oxide (I) (A., 1935, 1488) is shown to have the bond-structure of anthracene. It can be titrated with KI, which reduces it to anthranol or oxanthrol, but isomerisation and subsequent aërial oxidation to other products also occur. (I) resembles oxanthrone in state of oxidation and in giving with HCl and HBr 10-chloro- (II) and -bromo-anthrone, respectively. (II) melts on a block at 165° with loss of HCl and resolidification owing to immediate passage into *10-chloro-10 : 10′-dihydro-10 : 10′-dianthronyl*, m.p. 235°. The m.p., 225°, previously assigned to (II), is due to this transformation, which occurs appreciably even at 100°. 10-Halogenoanthrones are best identified by transformation into 10-methoxyanthrone, m.p. 103—104°. R. S. C.

Synthesis of mixed benzoins. II. R. T. Arnold and R. C. Fuson (J. Amer. Chem. Soc., 1936, **58**, 1295—1296; cf. A., 1935, 1499).—Condensation of arylglyoxals, COAr·CHO (Ar = $p\text{-}C_6H_4Cl{\cdot}$, b.p. 123—125°/17 mm., m.p. 40—42°; $p\text{-}C_6H_4Br{\cdot}$, b.p. 115°/7 mm., m.p. 51—52°), prepared by a slight modification of Riley and Gray's method (this vol., 471), with Ar′H by means of $AlCl_3$ (or, occasionally $ZnCl_2$) in absence or (usually) presence of CS_2 gives benzoins, COAr·CHAr′·OH (I) (35—90% yields), oxidised (method: Corson and McAllister, A., 1929, 1301) to COAr·COAr′. The following (I) are described: benzoin; benzoyl-anisyl-, *-naphthyl-*, m.p. 128°, -chlorophenyl-, *-bromophenyl-*, m.p. 125—126°, -tolyl-, and -mesityl-carbinols; *mesitoyl-mesityl-*, m.p. 59—60°, and -phenyl-carbinols; *p-bromobenzoylphenylcarbinol*, m.p. 108—109°; $p\text{-}C_6H_4Cl{\cdot}CO{\cdot}CHPh{\cdot}OH$; $C_6H_4Me{\cdot}CO{\cdot}CHPh{\cdot}OH$. *Ph $C_{10}H_7$ diketone*, m.p. 87°, is new. H. B.

Preparation of α-mono-oximes of aryl aliphatic diketones. C. Philipp (Annalen, 1936, **523**, 285—289).—COMe·CH:N·OH and acid diazonium solutions, best in presence of $CuSO_4$, give good yields of the α-oximes, OH·N:CMe·COR, in which R is Ph, $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4Cl$, $p\text{-}OMe{\cdot}C_6H_4$, $p\text{-}OEt{\cdot}C_6H_4$, and $\beta\text{-}C_{10}H_7$. The *α-oximes* of *p*-chlorophenyl and $\beta\text{-}C_{10}H_7$ Me diketone melt at 174° and 152°, respectively. R. S. C.

Preparation and properties of *o*-bromophenyl benzyl diketone. Methylation of α-diketones. R. P. Barnes and N. F. Payton (J. Amer. Chem. Soc., 1936, **58**, 1300—1302).—$o\text{-}C_6H_4Br{\cdot}COMe$ and PhCHO in aq. EtOH–NaOH at 15—20° give *o-bromophenyl styryl ketone* (I), b.p. 183—185°/2 mm. [*dibromide*, m.p. 86°, converted by 10% KI in $COMe_2$ into (I)], oxidised (30% H_2O_2, aq. EtOH–NaOH) to *o-bromophenyl benzyl diketone* (II), b.p. 155°/2 mm. [*quinoxaline*, m.p. 110°, from $o\text{-}C_6H_4(NH_2)_2$], which is 100% enolic in the solid *state*, m.p. 107° (III) [obtained by acidification of the red upper layer from (II) and aq. EtOH–NaOH]. (II) is cleaved by alkaline H_2O_2 in MeOH to $CH_2Ph{\cdot}CO_2H$ and $o\text{-}C_6H_4Br{\cdot}CO_2H$. Methylation ($Me_2SO_4$, aq. KOH) of (III) gives *o-bromophenyl α-methoxystyryl ketone*, b.p. 280—285°/2 mm. The amount of *O*-Me ether formed during methylation of an α-diketone is considered to be ∝ the acidity of the enol; COR·C(:CHR)·OH can be regarded as a glyoxylic acid with :O replaced by :CHR. β-Diketones cannot give such derivatives. $o\text{-}C_6H_4Br{\cdot}CO{\cdot}CO_2H$ has k^{25} $8{\cdot}6\times10^{-2}$. H. B.

Formation of cholestane-3 : 6-dione from cholestenone dibromide and from Δ^4- and Δ^5-cholestenone. Y. Urushibara and T. Ando (Bull. Chem. Soc. Japan, 1936, **11**, 434—436).—Cholestane-3 : 6-dione is formed by treatment of Δ^4- or Δ^5-cholestenone with an equiv. amount of Br in abs. EtOH. Cholesterol is regenerated from its dibromide in good yield by heating the latter in abs. EtOH. A. T.

Testosterone.—See this vol., 1156.

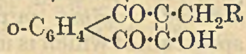
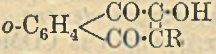
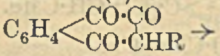
Displacement of the anisoyl group in the nitration of dimethoxybenzophenones. C. W. Pohlmann (Rev. trav. chim., 1936, **55**, 737—752).—Tetranitration of *oo*′- (I) or *pp*′-dimethoxybenzophenone (II) or of their NO_2-derivatives is accompanied by much replacement of the aroyl group by NO_2, forming dinitro-anisoles and -anisic acids. This does not occur with the *m*-OMe-compounds, since the aroyl is never *m*- to a NO_2. 10 g. of (II) with abs. HNO_3 at −15° (method *A*) give the 3 : 3′ : 5 : 5′-$(NO_2)_4$-derivative (III) 6·5, dimorphous, m.p. 182° and 197°, 2 : 4-$C_6H_3(NO_2)_2\cdot OMe$ (IV) 5·6, and 4 : 3 : 5-$OMe\cdot C_6H_2(NO_2)_2\cdot CO_2H$ (V) 1·75 g., and with HNO_3–Ac_2O at 0° (method *B*) 5 g. give (III) 0·3, (IV) 0·6, the 3 : 3′-$(NO_2)_2$-derivative (VI) of (II) 3·9, and 3 : 4-$NO_2\cdot C_6H_3(OMe)\cdot CO_2H$ (VII) 0·55 g. (VI) (2 g.) gives (III) 1·1, (IV) 0·65, and (V) 0·74 g. 2 g. of 3-*nitro*-4 : 4′-*dimethoxybenzophenone* [from PhOMe, 3 : 4-$NO_2\cdot C_6H_3(OMe)\cdot COCl$, and $AlCl_3$ in CS_2, not from *o*-$NO_2\cdot C_6H_4\cdot OMe$ and $OMe\cdot C_6H_4\cdot COCl$], m.p. 143°, gives by (*A*) (III) 0·95, (IV) 0·59, and 4 : 3 : 5-$OH\cdot C_6H_2(NO_2)_2\cdot CO_2H$ 0·69 g., or by (*B*) (III) 1·28, (IV) 0·13, and (VII) 0·13 g. (I) and Br–AcOH yield much 3 : 3′-*dibromo*- (VIII), m.p. 182°, and a little 3-*bromo*-4 : 4′-*dimethoxybenzophenone* (IX), m.p. 89° (also obtained from 4 : 3-$OMe\cdot C_6H_3Br\cdot COCl$ and PhOMe). (VIII) with HNO_3–H_2SO_4 gives only 2 : 4 : 6-$(NO_2)_2C_6H_2Br\cdot OMe$ (X) and by (*A*) 3 : 3′-*dibromo*-5 : 5′-*dinitro*-4 : 4′-*dimethoxybenzophenone*, m.p. 177°, and traces of (X) and 4 : 3 : 5-$OMe\cdot C_6H_2Br(NO_2)\cdot CO_2H$ (XI). (IX) (2 g.) gives by (*A*) 3-*bromo*-3′ : 5 : 5′-*trinitro*-4 : 4′-*dimethoxybenzophenone* (XII), m.p. 175° (1·24 g.), (XI) (0·83 g.), and (IV) (0·68 g.), or by (*B*) (1·5 g.) 3-*bromo*-3′-*nitro*-4 : 4′-*dimethoxybenzophenone* (XIII) (also obtained from the 3-NO_2-derivative and Br–AcOH), m.p. 166° (1·35 g.), 4 : 3-$OMe\cdot C_6H_3Br\cdot CO_2H$ (0·19 g.), and (IV) (0·17 g.). 1·4 g. of (XIII) gives by (*A*) (XII) 1·1, (XI) 0·29, and (IV) 0·18 g. (I) (3·5 g.) gives by (*B*) 5 : 5′-*dinitro*-2 : 2′-*dimethoxybenzophenone* (XV), m.p. 188° (2·44 g.; gives 2 : 7-dinitroxanthone with 75% H_2SO_4 at 150°), 2 : 5-$OMe\cdot C_6H_3(NO_2)\cdot CO_2H$ (1·11 g.; prep. from 5 : 2-$NO_2\cdot C_6H_3Cl\cdot CO_2H$ and MeOH), and *o*-$NO_2\cdot C_6H_4\cdot OMe$ (0·9 g.), and by (*A*) (2 g.) 3 : 3′ : 5 : 5′-*tetranitro*-2 : 2′-*dimethoxybenzophenone* (XVI), m.p. 175° (1·76 g.), (IV) (0·4 g.), 2 : 3 : 5-$OMe\cdot C_6H_2(NO_2)_2\cdot CO_2H$ (XVII) (0·64 g.), and 2 : 4 : 6-$C_6H_2(NO_2)_3\cdot OH$ (a trace). 0·6 g. of (XV) gives by (*A*) (XVI) 0·33, (IV) 0·14, and (XVII) 0·24 g. 3 : 3′-Dimethoxybenzophenone gives by (*A*) only the 4 : 4′ : 6 : 6′-$(NO_2)_4$-derivative, m.p. 231°, converted by HNO_3–H_2SO_4 at 100° into the 2 : 4 : 4′ : 6 : 6′-$(NO_2)_5$-derivative, m.p. 209°, and a trace of a substance, m.p. 143°. (XVI) with the appropriate base in EtOH at 100° gives 1 : 3 : 7 : 9-tetranitroacridone, m.p. 337° (block), and its 10-*Me*, m.p. 318° (block), -*Et*, m.p. 282° (block), -*Pr*^{a}, m.p. 273° (block), -*Bu*^{a}, m.p. 260° (block), -n-*amyl*, m.p. 195°, -n-*hexyl*, m.p. 174°, and -n-*heptyl*, m.p. 167°, derivatives. R. S. C.

***Paprika* dye. IX. Partial degradation of capsanthin.** L. Zechmeister and L. von Cholnoky (Annalen, 1936, **523**, 101—108).—Oxidation of capsanthin diacetate (I) with CrO_3 (≡ 2 O) gives unrecognised by-products, unchanged material, and *capsanthinone diacetate*, (II), m.p. 123—124° (corr.; block). Capsanthinone therefore contains 2 OH and 3 CO. Since it exactly resembles capsorubin in absorption spectrum it contains 2 CO in unbroken conjugation with 9 C:C linkings and an isolated CO and hence is $COMe\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CMe_2\cdot CO\cdot[CH:CH\cdot CMe:CH]_2\cdot[CH:CH\cdot CH:CMe]_2\cdot CH:CH\cdot CO\cdot CMe_2\cdot CH_2\cdot CHPr^a\cdot OH$. The presence of 2 CO in the αξ position is shown by the conversion of (II) by 10% KOH–MeOH at room temp. into *anhydrocapsanthione*, $C_{40}H_{56}O_4$, the spectrum of which is explained by the conjugation of the "isolated" CO with a newly-formed C:C. More drastic oxidation of (I) with CrO_3 leads to *capsanthylal*, m.p. 127° (corr.) [*oxime*, m.p. 184° (corr.)], which is shown spectroscopically to contain an unbroken sequence of 11 conjugated linkings and hence to be $CHO\cdot[CMe:CH\cdot CH:CH]_2\cdot[CH:CMe\cdot CH:CH]_2\cdot CO\cdot CMe_2\cdot CH_2\cdot CHPr^a\cdot OH$, *capsyl aldehyde* [*oxime*, m.p. 172° (corr.)], the absorption spectrum of which is identical with that of β-carotenone aldehyde and which is therefore $CHO\cdot CH:CH\cdot CMe:CH\cdot[CH:CH\cdot CH:CMe]_2\cdot CH:CH\cdot CO\cdot CMe_2\cdot CH_2\cdot CHPr^a\cdot OH$, and β-*hydroxycarotenone aldehyde* [*oxime*, m.p. 189° (corr.)] which is $COMe\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CMe_2\cdot CO\cdot[CH:CH\cdot CMe:CH]_2\cdot CH:CH\cdot CH:CMe\cdot CH:CH\cdot CHO$. The structure $OH\cdot CH{<}\begin{smallmatrix}CH_2\cdot CMe_2\\ CH_2-CMe\end{smallmatrix}{\gg}C\cdot[CH:CH\cdot CMe:CH]_2\cdot[CH:CH\cdot CH:CMe]_2\cdot CH:CH\cdot CO\cdot CMe_2\cdot CH_2\cdot CHPr^a\cdot OH$ may therefore be ascribed to capsanthin (III) in which the cyclic system, the OH, 18 C atoms, and position of CO are assured. Treatment of (III) with KOH–EtOH–MeOH–H_2O at 70—80° in absence of air is a practicable method for its degradation; a cryst. *substance*, m.p. 112° (corr.), has been isolated. H. W.

Reaction between toluoquinone and cinnamaldehyde under the influence of light. A. Angeletti (Atti R. Accad. Sci. Torino, Cl. Sci. fis., 1934—5, **70**, I, 326—330; Chem. Zentr., 1935, ii, 2945).—Cinnamic acid, 2-methylquinol, and (probably) 4-*hydroxy*-3-*methylphenyl cinnamate*, m.p. 163°, are formed. H. N. R.

Condensation of aldehydes with 2-hydroxy-1 : 4-naphthaquinone. Synthesis of hydrolapachol. S. C. Hooker (J. Amer. Chem. Soc., 1936, **58**, 1163—1167; cf. J.C.S., 1896, **69**, 1356).—The following 3-hydroxy-2-Δ^a-alkenyl-1 : 4-naphthaquinones (*A*) are obtained from 2-hydroxy-1 : 4-naphthaquinone and RCHO in AcOH–conc. HCl at 75—80°: *propenyl* (I), m.p. 135·2—135·7° (accompanied by a little of a *compound*, m.p. 160—160·5°), *butenyl* (II), m.p. 107·5° (*acetate*, m.p. 83·5—84°), *pentenyl*, m.p. 98—98·5°, *heptenyl*, m.p. 86·5°, *styryl*, m.p. 166·5—167·5° (*acetate*, m.p. 138·7—139·2°, red and orange-yellow forms), and γ-*phenylpropenyl* (III), m.p. 140·5—141·5° (decomp.). (*A*) could not be prepared from MeCHO and Pr^{β}CHO. (I) heated in EtOH decomposes to a *compound*, m.p. 197—198° (decomp.); an EtOH-solution of (II) slowly deposits a *substance*, m.p. 207—208° (decomp.), whilst (III) undergoes autoxidation in C_6H_6 to a *compound*, ? $C_{19}H_{14}O_4$, m.p. 227—228° (decomp.). Reduction (H_2, PtO_2, EtOH) of (*A*) and, in some cases, the isomeric Δ^β-alkenyl derivatives (Fieser, A., 1927, 155, 462) followed by atm. oxidation, gives the 3-*hydroxy*-2-*alkyl*-1 : 4-*naphthaquinones*: the *Pr*^{a}, m.p. 100·5—101·5°, *Bu*^{a}, m.p. 101—101·5°, n-*amyl*, m.p. 104—104·3°, n-*heptyl*, m.p. 82·7—83·3°, β-

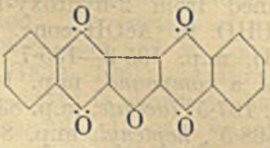
phenylethyl, m.p. 171·5—172·5°, and *γ-phenylpropyl*, m.p. 131·7—132·2°, derivatives are described. 3-Hydroxy-2-γ-methyl-Δ^{α}-butenyl-1 : 4-naphthaquinone (*iso*lapachol) (cf. *loc. cit.*) is similarly reduced to the 2-iso*amyl* derivative (hydrolapachol), m.p. 93·5—94·5° (lit. 87—89°), identical with the reduction product of lapachol. H. B.

Oxidation of 2-hydroxy-1 : 4-naphthaquinone derivatives with alkaline potassium permanganate. [I. Mechanism.] S. C. Hooker. **II. Compounds with unsaturated side-chains.** S. C. Hooker and A. Steyermark (J. Amer. Chem. Soc., 1936, 58, 1174—1179, 1179—1181).—I (cf. Fieser *et al.*, below). Oxidation of  $o\text{-}C_6H_4{<}^{CO\cdot C\cdot CH_2R}_{CO\cdot C\cdot OH}$ (I) (R=H, Me—hexyl, Ph,·CH_2Ph, and ·CH_2·CH_2Ph) with $KMnO_4$ (= >2 O) in aq. NaOH in absence or presence of air gives  $o\text{-}C_6H_4{<}^{CO\cdot C\cdot OH}_{CO\cdot CR}$ (II) in (usually) 70—96% yield. Reaction probably occurs thus : (I) → o-CO_2H·CO·C_6H_4·CO·CH_2R → CO_2+o- $C_6H_4{<}^{CO\cdot CO}_{CO\cdot CHR}$ → (II). The same reaction also occurs when R is unsaturated. 3-*Hydroxy*-2-*ethyl*-, m.p. 138·2—138·7°, and -2-n-*hexyl*-, m.p. 98—98·5°, -1 : 4-*naphthaquinones* are new. 2-Hydroxy-1 : 4-naphthaquinone and its saturated derivatives give a dark blue colour with conc. H_2SO_4 and C_6H_6 containing thiophen.

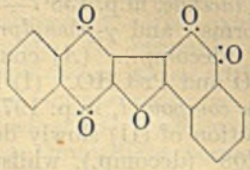
II. 3-Hydroxy-2-allyl-, -2-γ-methylallyl-, and -2-cinnamyl-1 : 4-naphthaquinones are similarly oxidised (usually in more dil. NaOH) to 3-*hydroxy*-2-*vinyl*-, m.p. 121·5—123·5°, -2-Δ^{α}-propenyl-, and -2-styryl-1 : 4-naphthaquinone, respectively. H. B.

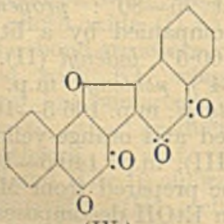
Action of light on 2-hydroxy-1 : 4-naphthaquinone. S. C. Hooker (J. Amer. Chem. Soc., 1936, 58, 1212—1216).—Exposure of dil. aq. solutions of 2-hydroxy-1 : 4-naphthaquinone (improved prep.) at 70° to light from a "Uviarc" lamp gives *iso*-naphthazarin and (mainly) 3 : 3′-*dihydroxy*-2 : 2′-*dinaphthyl*-1 : 4 : 1′ : 4′-*diquinone* (I), m.p. about 270—275° (decomp.) (sublimes from 250°), converted by AcOH–dil. H_2SO_4 into the *anhydride* (II), m.p. 349—350° (Berl block), and a little of the *anhydride* (III), m.p. 317—318° (decomp.) (block) [*quinoxaline*, m.p. 329—330° (block)]. (I) and conc. H_2SO_4 at room temp. give (III) and a little of the *anhydride* (IV), decomp. 335—345° (*diquinoxaline*, m.p. 409—410°), whilst (I) and Ac_2O–NaOAc or –H_2SO_4 afford (IV) only. Tetra-acetoxydinaphthyl is a by-product in the prep. (method : Thiele and Winter, A., 1900, i, 504) of 1 : 2 : 4-$C_{10}H_5(OAc)_3$. H. B.

(II.)



(III.)

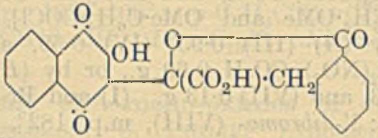




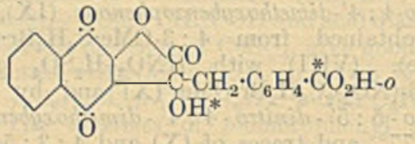
(IV.)

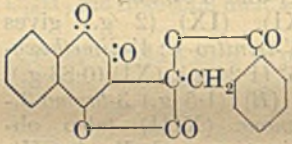
Wichelhaus' "di-β-naphthaquinone oxide." S. C. Hooker and L. F. Fieser (J. Amer. Chem. Soc., 1936, 58, 1216—1223).—1 : 2-Naphthaquinone is oxidised by aq. $FeCl_3$ at 65—70° (bath) to 1 : 1′-dinaphthyl-3 : 4 : 3′ : 4′-diquinone and (mainly) 3-*hydroxy*-2 : 2′-*dinaphthyl*-1 : 4 : 3′ : 4′-*diquinone* (I), m.p. 253—254° (decomp.) (darkens about 240°) (*acetate*, m.p. 205—205·5°). (I) is the "di-β-naphthaquinone oxide" of Wichelhaus (A., 1898, i, 33). Distillation of (I) with Zn dust gives 2 : 2′-dinaphthyl, whilst oxidation (evaporation of solution in 6% NaOH at room temp. in air) affords the *lactonic acid* (II), m.p. 203—205° (decomp.) (softens about 201°) [*Me*$_2$ derivative (CH_2N_2), m.p. 225—226° (softens about 220°)], which is converted by boiling AcOH into the *lactonic acid* (III), m.p. 264° (decomp.; after loss of H_2O) [*Me*$_2$ ester, m.p. 249—250° (previous softening)], also formed from (I) and 30% H_2O_2 in AcOH. (III) heated in xylene affords the corresponding *dilactone*, m.p. 264°, by loss of H_2O between **. (II) is dehydrated by conc. H_2SO_4 at room temp. to the *dilactone* (IV), m.p. 248—249·5°, hydrolysed (1% NaOH) to (III). (II) heated with EtOH gives (III) and the *lactone* (V), m.p. 177·5—178° [better obtained from (II) and Cu powder in C_5H_5N] [*Me*$_1$ derivative (CH_2N_2), m.p. 165—166°], converted by cold conc. H_2SO_4 into an *anhydro*-derivative, $C_{19}H_{10}O_4$, decomp. about 220—225°.

(II.)

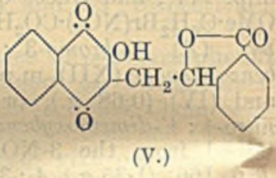


(III.)





(IV.)



(V.)

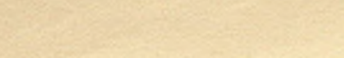
1 : 2′-Dinaphthyl, m.p. 72—73° [*dipicrate*, m.p. 127—127·5° (corr.)] (cf. Smith, J.C.S., 1879, **35**, 227) is obtained by dehydrogenation (S at 230—250°) of the distilled product, b.p. 217—219°/3 mm., from β-$C_{10}H_7$·MgBr and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. H. B.

Mechanism of the Hooker oxidation. L. F. Fieser, J. L. Hartwell, and A. M. Seligman (J. Amer. Chem. Soc., 1936, **58**, 1223—1228).—The following results confirm Hooker's view (see above) that oxidation of 2-hydroxy-3-alkyl- (or aralkyl-)1 : 4-naphthaquinones involves fission of the quinone ring and subsequent ring closure in a different manner, so that the 2- and 3-substituents exchange positions. 6-*Bromo*-1 : 2 : 4-*triacetoxynaphthalene*, m.p. 162° (from 6-bromo-1 : 2-naphthaquinone and Ac_2O–H_2SO_4), is hydrolysed (EtOH–KOH) and oxidised (air) to 6-bromo-2-hydroxy-1 : 4-naphthaquinone (I), m.p. 204—205°, which with $CH_2Ph\cdot CHO$ in AcOH–conc. HCl at 80° gives 6-*bromo-2-hydroxy-3-styryl*-1 : 4-*naphthaquinone*, m.p. 243—244° (corresponding *quinol triacetate*, m.p. 197—198°), reduced (H_2, PtO_2, EtOH) to 6-*bromo*-2-*hydroxy*-3-β-*phenylethyl*-1 : 4-*naphthaquinone* (II), m.p. 180—181° (*quinol triacetate*, m.p. 188—189°). (I) and $CH_2Ph\cdot CH_2\cdot CHO$ similarly afford 6-*bromo*-2-*hydroxy*-3-γ-*phenyl*-Δ^{α}-*propenyl*-1 : 4-*naphthaquinone*, m.p. 177—178°; the *quinol triacetate*, m.p. 170—171°, from this is reduced (Adams) to 6-*bromo*-1 : 2 : 4-*triacetoxy*-3-γ-*phenylpropylnaphthalene*, m.p. 170—172°, which is hydrolysed (EtOH–KOH in air) to 6-*bromo*-2-*hydroxy*-3-γ-*phenylpropyl*-1 : 4-*naphthaquinone* (III), m.p. 170—171°. The Ag salt of (I) with CH_2PhBr in Et_2O gives 6-*bromo*-4-*benzyloxy*-1 : 2-*naphthaquinone*, m.p. 227—228°, 6-*bromo*-2-*hydroxy*-3-*benzyl*-1 : 4-*naphthaquinone* (IV), m.p. 192° (*quinol triacetate*, m.p. 202—203°), and 6-*bromo*-2-*benzyloxy*-1 : 4-*naphthaquinone*, m.p. 201—202°. Oxidation (1% $KMnO_4$) of (III) (in 1% NaOH+C_6H_6) at 0° affords 6-*bromo*-3-*hydroxy*-2-β-*phenylethyl*-1 : 4-*naphthaquinone*, m.p. 173—175° [which differs from (II)], further oxidised to (IV). Similar oxidation of (II) gives 6-*bromo*-3-*hydroxy*-2-*benzyl*-1 : 4-*naphthaquinone*, m.p. 158—159° (*quinol triacetate*, m.p. 196—197°), which differs from (IV). 3-Hydroxy-2-*iso*butyl-1 : 4-naphthaquinone (*acetate*, m.p. 53·5—54°) is similarly oxidised to the -2-iso*propyl*-derivative, m.p. 92—93°, and thence (by way of *o*-$CO_2H\cdot CO\cdot C_6H_4\cdot CO\cdot COPr^{\beta}$) to *o*-$CO_2H\cdot C_6H_4\cdot CO\cdot CO_2H$ and $Pr^{\beta}CO_2H$. 3-Hydroxy-2 : 6-dimethyl-1 : 4-naphthaquinone is oxidised in a more strongly alkaline medium to 2-*hydroxy*-6-*methyl*-1 : 4-*naphthaquinone*, m.p. 199° (decomp.) [*Me ether* (V), m.p. 167—167·5°; *quinol triacetate*, m.p. 157—158°]. Reduction ($Na_2S_2O_4$) of the dye from diazotised *p*-$NH_2\cdot C_6H_4\cdot SO_3H$ and 6 : 2-$C_{10}H_6Me\cdot OH$ (VI) affords 1 : 6 : 2-$NH_2\cdot C_{10}H_5Me\cdot OH$, which is oxidised ($K_2Cr_2O_7$, dil. H_2SO_4) to 6-methyl-1 : 2-naphthaquinone, m.p. 126°. Successive treatment of this with $NaHSO_3$, boiling dil. H_2SO_4, $K_2Cr_2O_7$–dil. H_2SO_4, and KCl gives *K* 6-*methyl*-1 : 2-*naphthaquinone*-4-*sulphonate* (+H_2O), converted by MeOH–conc. H_2SO_4 into (V). *o*-$C_6H_4(CO)_2O$, (VI), and $AlCl_3$ at 200° yield 1 : 8-*phthaloyl*-6-*methyl*-β-*naphthol* (1-*hydroxy*-5-*methylpleiadenedione*), m.p. 194—194·5°, rearranged by 2 : 1 (vol.) H_2SO_4–H_2O at 170° into 2′-*hydroxy*-4-*methyl*-1 : 2-*benzanthraquinone*, m.p. 256—258° (decomp.) (*acetate*, m.p. 218—219°). H. B.

Chrysene. III. K. Funke and J. Ristic (J. pr. Chem., 1936, [ii], **145**, 309—312; cf. this vol., 472).—8-Benzoylchrysene-1 : 2-quinone gives a *phenazine* derivative, m.p. 207°, proving the structure of the quinone. 2-Acetylchrysene and $Na_2Cr_2O_7$–AcOH give *chrysene*-1 : 2-*quinone*-8-*carboxylic acid*, m.p. 297° (*phenazine* derivative, m.p. >330°). 2 : 8-Dibromochrysene with CrO_3–AcOH gives a small amount of a Br-free *substance*, m.p. 323—324°, but with $Na_2Cr_2O_7$–AcOH affords 8-*bromochrysene*-1 : 2-*quinone*, m.p. 249—250° (*phenazine* derivative, m.p. 252°), which proves the orientation. 1- or 2-Substituted chrysene derivatives afford by oxidation 8- or 7-substituted 1 : 2-quinones, and derivatives substituted in the 1 or 2 and 7 or 8 positions give similar quinones if one substituent is readily removed. 2 : 8-Dicyanochrysene is stable to oxidising agents and affords no quinone. R. S. C.

Anthanthrone and its derivatives. VII. Halogenation, nitration, and sulphonation of anthanthrone. A. Corbellini and M. Atti (Chim. e l'Ind., 1936, **18**, 295—298).—Anthanthrone (I) is chlorinated by SO_2Cl_2 in $PhNO_2$, and is brominated (cf. G.P. 458,598) to the Cl- and Br-derivatives, $C_{22}H_8O_2X_2$. Iodination (G.P. 495,367) yields an impure I-derivative, containing <1 atom of I per mol. of (I). Nitration (G.P. 492,446) yields nitro- and dinitro-, decomp. 360°, -anthanthrone, from which the NH_2- and $(NH_2)_2$-compounds are prepared. Sulphonation (oleum) gives *anthanthrone-sulphonic acid*, from which the -*sulphonyl chloride*, m.p. 306·5—307·5°, is prepared, with disulphonyl compounds.
E. W. W.

Woolly aphis and white pine chermes.—See this vol., 1137.

Pinic acid. M. Grandperrin (Ann. Chim., 1936, [xi], 6, 5—52).—Evidence is adduced in favour of the view that pinic acid obtained by the oxidation of pinonic acid in alkaline solution has the *trans*-configuration. *d*-α-Pinene, $[\alpha]_D$ +42°, is oxidised by $KMnO_4$ in H_2O containing $(NH_4)_2SO_4$ at 0° to pinonic acid (I), $[\alpha]_D$ +95°; oxidation by $KMnO_4$ in $COMe_2$ appears more suited to the formation of neutral products. Oxidation of (I) by Br in alkaline solution gives CBr_4, $CHBr_3$, and an acid which only becomes partly cryst. after long keeping (oxidation with H_2O_2 or $K_2Cr_2O_7$ in AcOH gives less satisfactory results whereas treatment with HNO_3 appears to give terebic acid). Crystallisation of the crude acid without distillation, which involves risk of racemisation, leads to pinic acid (II), m.p. 78—79°, $[\alpha]_D$ +10·6° in Et_2O, −1·9° in $CHCl_3$, +5·1° in $COMe_2$, −4° in H_2O. (II) is transformed by $SOCl_2$ into the *dichloride* (III), b.p. 141—142°/15 mm., $[\alpha]_D$ −41·5°, whence *Et_2 pinate* (IV), b.p. 148—149°/15 mm., $[\alpha]_D$ +3·36° (also obtained from *Ag_2 pinate* and EtI), *Pr^{β}_2 pinate* (V), b.p. 161°/20 mm., [α] +1·36°, and *Bu^{β}_2 pinate*, b.p. 181°/22 mm., [α] −0·48′. (III) is converted by NH_3–EtOH into *pindiamide*, m.p. 190°, by NH_2Ph into the *dianilide*, m.p. 208°, by the requisite amount of EtOH followed by NH_2Ph into the *ester anilide*, m.p. 92° (with a non-identified product, m.p. 248°), and by *p*-$OMe\cdot C_6H_4\cdot NH_2$ into the *di*-p-*anisidide*, m.p. 202°. (IV) and (V) are converted by MgEtBr into the corresponding di-*tert*.-glycols which could not be isolated free from their products of dehydration. Attempts to prepare pinic anhydride from (II) and AcCl, from (III) and Na_2 pinate, or from (III) and Ag_2O were unsuccessful. Similarly the imide, anil, or anisidil could not be obtained. A ketonic ester is not formed by the action of $NaNH_2$ on (IV). Dehydration of the crude di-*tert*.-glycol by H_2SO_4–pumice or 2-$C_{10}H_7\cdot SO_3H$ and purification of the product with H_3BO_3 leads to the *hydrocarbon*,  $CEt_2{:}C\!<\!\begin{matrix}CMe_2\\CH_2\end{matrix}\!>\!CH{:}CH{:}CEt_2$, b.p.

148—149°/22 mm. Isomerisation of (II) under the action of Ac_2O is not observed. H. W.

Preparation and properties of pinonic acid. M. Delépine (Bull. Soc. chim., 1936, 3, [v], 1369—1382).—Optically active pinonic acid (I) (prep. described) in KOH or when heated shows a rapidly decreasing α owing to a *cis–trans* unimol. change; in aq. NH_3 the change is 1/600 times as fast. The change is not one of racemisation but of mutarotation (much lit. cited). The action of alkali affords the pure *trans*-acid, $[\alpha]_D$ +95° in $CHCl_3$, and an oil which is a *trans–cis* mixture with a lower $[\alpha]_D$ increased by treatment with alkali. The semicarbazone (II), $[\alpha]_D$ +90°, of (I) gives an Ac derivative which when pptd. from alkaline solution yields (II); the mother-liquors contain a semicarbazone, $[\alpha]_D$ −88°, which when hydrolysed affords a *trans*-acid with $[\alpha]_D$ −77°. The *cis*- and *trans-d*-acids give oximes, m.p. 128° and 191°, respectively, whilst the *l*-acids give oximes, m.p. 191° and 128°, respectively. J. L. D.

Preparation of monoalkyl and aryl derivatives of β-campholide and of the corresponding δ-hydroxy-acids. J. Vène (Compt. rend., 1936, 202, 1681—1683).—Me camphoceanaldehydate CHO(β)·C_8H_{14}·CO_2Me(α) (cf. A., 1917, i, 560; 1932, 1037) with MgRX affords β-substituted campholides (I). The following are prepared: β-*methyl*-, m.p. 178°, -*ethyl*-, m.p. 78°, -*propyl*-, impure, -*butyl*-, b.p. 179—181°/16 mm., -*phenyl*-, m.p. 212°, and -*benzyl-campholide*, m.p. 102°. In attempting to prepare the higher aliphatic homologues, (I) tends to be converted into β-campholide. (I) with NaOH–EtOH at 100° give OH-acids (II) of which the following are prepared: 2 : 2 : 3-*trimethyl*-3-α-*hydroxyethyl*-, m.p. 135°, -3-α-*hydroxypropyl*-, m.p. 73° (+xH_2O, m.p. 86°), -3-α-*hydroxybenzyl*-, m.p. 166°, -3-(α-*hydroxy*-β-*phenylethyl*)-cyclo*pentane*-1-*carboxylic acid*, m.p. 154°. (II) with Ac_2O or when heated give (I). J. L. D.

Action of selenium dioxide on camphene and pinene. W. Zacharewicz (Rocz. Chem., 1936, 16, 290—300).—Pinene and SeO_2 in EtOH at 60° yield myrtenol (I) and myrtenal [identified wrongly as verbenol and verbenone by Schenk *et al.* (A., 1932, 1253) and Dupont *et al.* (A., 1933, 1166)], formed by decomp. of *dimyrtenyl selenide* (II), m.p. 64—65°. (II) and Br in $CHCl_3$ at 0° yield myrtenyl iodide, identified by conversion into (I). Camphene and SeO_2 yield camphenilone and *iso*borneol in small amount, but the chief product is *di*-3-*camphenyl selenide*, b.p. 220—225°/8 mm., m.p. 93—94°, from which camphene is regenerated by Walbaum's reaction. R. T.

(A) **Products of oxidation of hydrazones of camphorquinone and 4-methylcamphorquinone.** (B) **Nitrogenous derivatives of 4-methylcamphor.** L. Briusova (J. Gen. Chem. Russ., 1936, 6, 667—673, 674—680).—(A) β-*pericyclo*Camphanone (I) is regenerated from its *hydrazone*, m.p. 76·5—77·5°, by heating at 50—70° with HgO in EtOH; when the reaction is performed in a CO_2 atm. in presence of I the 2 : 2-I_2-derivative, m.p. 160—162°, of (I) is also produced. The *dihydrazone* (impure), m.p. 101—104° (*hydrochloride*, m.p. 177—180°), of 4-methylcamphorquinone (II) yields 4-methylcyclene when oxidised with HgO, and the *dihydrazone*, m.p. 196—198°, of camphorquinone gives tricyclene with HgO.

(B) The reactions of 4-methylcamphor (III) are on the whole analogous to those of camphor. 3-*Amino-4-methylcamphor*, m.p. 164—167° (*Ac* derivative, m.p. 127—128°, +H_2O, m.p. 84—86°; *carbonate*, m.p. 152—155°; *hydrochloride*), is prepared by reducing 3-*oximino-4-methylcamphor* (Zn–AcOH), whilst oxidation with $KMnO_4$ in $COMe_2$ yields 3-*nitro-4-methylcamphor*, m.p. 152—153°. The oxime of (III) and HNO_2 afford the *nitroimine*, m.p. 52—53·5°, which with NH_3 at 50° yields the *imine*, m.p. 64—67°. The *nitroimine*, m.p. 57·4—58·4°, of (II), obtained analogously, yields (II) when treated with EtOH–KOH, and the *dioxime*, m.p. 181—182°, of (II) with NH_2OH (100°; 30 min.). R. T.

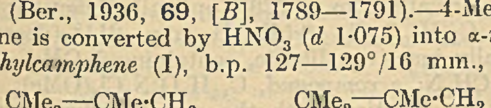
Preparation of optically active *trans*-π-hydroxycamphor from optically active απ-*trans*-dihalogenocamphor.—See B., 1936, 687.

Optical superposition. H. Rupe, F. Henke, and F. Bürki (Helv. Chim. Acta, 1936, 19, 698—734).—[With H. Hirschmann]. All except the first two pages of the paper by Rupe, Bürki, and Werdenberg (A., 1929, 529) are incorrect.

$[M]_D^{20}$ are determined for esters of *l*-, *d*-, and *dl*-hydroxymethylenecamphor (I) and -camphenylcarbinol (II) with *l*-, *d*-, and *dl*-bornylenecarboxylic (III) and -camphanecarboxylic acid (IV). $[M]$ of the esters is not the sum of $[M]$ of the free alcohols and acids. When both alcohols and acids are saturated, $[M]$ of the esters is the sum of $[M]$ of the alkyl and acyl radicals, but, when either is unsaturated or, more, so, if both are unsaturated, "polar" effects nullify this equality, so that the simple law of optical superposition no longer holds. Hydrogenation of the unsaturated esters gives only one stereoisomeride in each case; esters with different types of unsaturation give different stereoisomerides of the saturated esters owing to the formation of new asymmetric C. $[M]$ of these forms conforms to the above-mentioned law when the contribution of each asymmetric centre is taken into account. It is shown how these contributions can be calc. from the $[M]$ of the esters isolated. (I) is best obtained by the use of Na, since NH_2Na gives also much hydroxymethylenecamphorimide. The dl-*form* of (II) has b.p. 142°/11 mm. (*benzoate*, m.p. 73°); the l-*form* is also prepared. Esters of (I) are obtained by treating the dry *Na* salt (prep. by NaOMe) in C_6H_6 with the *chlorides*, b.p. 110—111°/11 mm. and 107—108°/11 mm., of (III) and (IV), respectively. In most cases (I) gives only one ester (assumed to be the stable *trans*-form) under the conditions used; the *cis*-forms are the more readily reduced and have the higher m.p.; this leads to configurations in agreement with the calc. vals. of $[M]$. Esters of (II) are prepared by the acid chloride in C_5H_5N (1·5 parts). Hydrogenation of esters of (I) is effected by Pd–H_2 in EtOH at 1 or 60—80 atm., as Ni leads to much hydrolysis to camphor with or without further reduction to methylcamphor; esters of (II) are smoothly reduced by H_2–Ni. The following *esters* are prepared, indicated by their components, *e.g.*, d-*hydroxymethylenecamphor* d-*bornylenecarboxylate* as *d*-(I)-*d*-(III), the angles recorded being $[\alpha]_D^{20}$ in C_6H_6. *d*-(I)–*d*-(III) (*A*), m.p. 119·5°, +215·54°; *d*-(I)–*dl*-(III), m.p. 131·5°, +104·31°; *l*-(I)–*d*-(III), trans-, m.p. 113·5°, −34·11°, and cis-*form*, m.p. 143·5°, −61·66°; *dl*-(I)–*d*-(III), m.p. 110·5°, +91·23°; *d*-(I)–*d*-(IV), trans-, m.p. 147·5°, +164·62°, and cis-*form*, m.p. 163·5°, +143·86°; *d*-(I)–*dl*-(IV), m.p. 155·5° +100·5°; *l*-(I)–*d*-(IV), trans-, m.p. 147°, −36·6°, and cis-*form*, m.p. 164°, −45·11°; *dl*-(I)–*d*-(IV), m.p. 150·5°, +76·69°; *d*-(II)–*d*-(III), m.p. 110°, +88·93°; *d*-(II)–*dl*-(III), m.p. 114°, +28·63°; *l*-(II)–*d*-(III), m.p. 114°, +46·19°; *l*-(II)–*dl*-(III), m.p. 114°, −25·96°; *l*-(II)–*l*-(III), m.p. 110°, −90·08°; *dl*-(II)–*d*-(III), m.p. 110°, +72·15°; *dl*-(II)–*l*-(III), m.p. 112°, −70·93°; *d*-(II)–*d*-(IV) (*B*), m.p. 157·5°, +55·94°; *d*-(II)–*dl*-(IV), m.p. 158°, +25·84°; *l*-(II)–*d*-(IV), m.p. 160°, +3·64°; *dl*-(II)–*d*-(IV), m.p. 152°, +28·42°; *dl*-(II)–*l*-(IV), m.p. 158°, −31·22°. *Esters*, (III)–(IV), were obtained by hydrogenation as follows: from (*A*), m.p. 179°, +103·61°; from *trans*-, m.p. 182°, −68·38°, and *cis*-*l*-(I)–*d*-(III), m.p. 179·5°, −51·92°; from *dl*-(I)–*d*-(III), m.p. 180°, +30·55°; from *trans*-, m.p. 165°, +67·61°, and *cis*-*d*-(I)–*d*-(IV), m.p. 167°, +106·14°; from *trans*-, m.p. 142°, −30·34°, and *cis*-*l*-(I)–*d*-(IV), m.p. 168°, −39·04°; from *dl*-(I)–*d*-(IV), m.p. 161°, +43·07°; (*C*) from *d*-(II)–*d*-(III), m.p. 163·5°, +54·39°; from *d*-(II)–*dl*-(III), m.p. 167°, +24·28°; from *l*-(II)–*d*-(III), m.p. 164°, +16·78°; from *l*-(II)–*dl*-(III), m.p. 166·5°, −21·37°; from *l*-(II)–*l*-(III), m.p. 163·5°, −56·39°; from *dl*-(II)–*d*-(III), m.p. 172°, +38·37°; and from *dl*-(II)–*l*-(III), m.p. 162·5°, −37·39°. Mutarotation of *l*-(I) is much faster than that of *d*-(I), increasing in speed with time in both cases; no explanation can be offered. In spite of the difference in m.p. (*B*), obtained by direct esterification, is identical with (*C*), obtained by reduction, since both have the same [α] and both, when hydrolysed, give the same (IV), m.p. 91°, [α] +74°. Hydrolysis of *d*-(II)–*dl*-(IV) gives *dl*-(IV), showing that no resolution takes place during esterification. Hydrolysis of the ester obtained by reduction of (*A*) gives a *form* of (IV), m.p. 91°, [α] +54·66°. α is determined for the esters for six λ; esters of (II), but remarkably not those of (I), show anomalous dispersion, particularly if log $[\alpha]\lambda^2$ is plotted against ν^2. R. S. C.

***sec*.-α-Nitro-4-methylcamphene and 4-methyl-α-camphenone.** S. S. Nametkin and A. S. Zabrodina (Ber., 1936, **69**, [*B*], 1789—1791).—4-Methylcyclene is converted by HNO_3 (*d* 1·075) into α-*nitro*-4-*methylcamphene* (I), b.p. 127—129°/16 mm., m.p.

(I.)



(II.)

40—40·5°, whence the ψ-*nitrol*, m.p. 91—92° (decomp.). (I) is transformed by cautious oxidation with $KMnO_4$ in alkaline solution into 4-*methyl*-α-*camphenone* (II), m.p. 129—130° [*semicarbazone*, m.p. 211—212° (decomp.)], also obtained in small yield by Sn and fuming HCl. H. W.

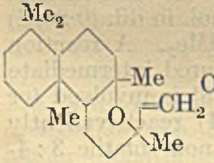
***exo*-2-*o*-Carboxybenzoylcamphane and *endo*-*cyclo*phthaloylcamphane.** R. Bousset (Bull. Soc. chim., 1936, [v], **3**, 871—875).—The acid, m.p. 154° (this vol., 206), may be separated by repeated crystallisation and by hydrolysis (cold) of its Me ester into two geometrical isomerides. The one, exo-2-o-*carboxybenzoylcamphane*, has m.p. 182° (corr.), $[\alpha]_J$ +89·20°, and the other, not yet obtained pure, readily cyclises in presence of alkalis to *endocyclo*-phthaloylcamphane, m.p. 216° (cf. *ibid*., 475). H. G. M.

Use of 2 : 4-dinitrophenylhydrazine. O. Fernández and M. Castillo (Anal. Fís. Quím., 1935, **33**, 81—89).—A quant. study of the formation of the dinitrophenylhydrazones (I) of the following camphor derivatives: α-*carboxylic acid*, m.p. 173°, β-*sulphonic acid*, yellow form, m.p. 215°, $[\alpha]_D$ −130° in dil. EtOH, red form, m.p. 193—195°, $[\alpha]_D$ 0°, α-*cyano*-, m.p. 225°, α-*hydroxy*-, yellow form, m.p. 225°, $[\alpha]_D$ +252° in dil. EtOH, red form, m.p. 225°, $[\alpha]_D$ +265° in EtOH, α-*acetoxy*-, m.p. 183°, α-*methoxy*-, m.p. 171°, α-*acetamido*-, m.p. 226·5°. α-*Acetamidocamphor*, m.p. 121°, was obtained from the free base. Br, NO_2, SO_3H, and NH_2 in the α-position prevent formation of (I). The difference between the red and yellow forms is discussed. F. R. G.

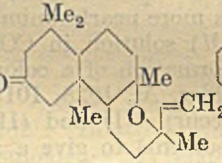
Mechanism of diene synthesis. E. R. Littmann (J. Amer. Chem. Soc., 1936, **58**, 1316—1317).—Reaction between α-phellandrene (I) and maleic anhydride (II) is more nearly unimol. in dil. (0·25*M*) than in conc. (*M*) solution in $COMe_2$. A reaction other than the formation of a coloured intermediate (cf. Diels and Alder, A., 1928, 1018) is involved (or side reactions occur). (I) and (II) react violently at 55—65° (no solvent) to give a non-volatile 3 : 4- or 4 : 5-*polymeride* of the type $C_4H_2O_3(C_{10}H_6–C_4H_2O_3)C_4H_2O_3$. H. B.

Pyronenes. G. Dupont and R. Dulou (Compt. rend., 1936, **202**, 1861—1863).—Conjugation of the ethylenic linkings of the pyronenes (A., 1935, 1127) is shown by the following reactions. The figures in parentheses are the frequencies of the lines of the Raman spectra. α- (I) (*nitrosochloride*, m.p. 103°) and β-pyronene (II) show predominently a line with frequency 1595 in the Raman spectra. Reduction of (I) by Na–EtOH gives a mixture of two hydrocarbons (1671, due to an intra-annular ethylenic linking attached to a *tert*.-C). Hydrogenation of (I) in presence of Raney Ni leads to absorption of 2 H and disappearance of the characteristic line (1595), and formation of a mixture of three hydrocarbons (1673, 1658, and 1647, respectively). Absorption of 2 H in presence of Pt gives from (I) a H_2-derivative (630, 666, 841, 998, 1264, 1377, and 1674), also obtained with carvomenthene (1673) from (II) similarly or by H_2–Ni or Na–EtOH. *dl*-(II) (from *dl*-pinene) with CH_2:CH·CHO at 110° gives an *adduct*, $C_{12}H_{19}$·CHO, b.p. 123°/15 mm. (*semicarbazone*, m.p. 209—210°), and with maleic anhydride in boiling C_6H_6 a product, hydrolysed to an *acid*, $C_{12}H_{18}(CO_2H)_2$, m.p. 154°. *dl*-(I) gives similarly an *aldehyde* (1116, 1184, 1270, 1627) and an *acid*, m.p. 195°. R. S. C.

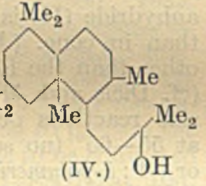
Chemistry of the genus *Dacrydium*. I. Resin of *D. Colensoi*. II. Diterpene alcohol from *D. biforme* wood. J. R. Hosking and C. W. Brandt (New Zealand J. Sci. Tech., 1936, **17**, 750—755, 755—758).—I. The resin from *D. Colensoi* gives 90% of neutral substances, which may be separated into manoyl oxide (I), $C_{20}H_{34}O$, m.p. 29°, a diterpene oxide, ketomanoyl oxide (II), $C_{20}H_{32}O_2$, m.p. 76°, a ketonic diterpene oxide, and a diterpene oxide (III), $C_{20}H_{32}O_4$, m.p. 208° (3 OH). (I) absorbs the equiv. of 1 H_2, shows stability of O, is dehydrogenated (Se) to 1 : 5 : 6-$C_{10}H_5Me_3$ and 1 : 7 : 8-trimethylphenanthrene, and with HCO_2H gives *iso*manoene, $C_{20}H_{32}$, containing 2 double linkings. With HCl, (I) yields a stable trihydrochloride, $C_{20}H_{35}Cl_3$, from which the Cl could not be removed, and dihydromanoyl oxide similarly forms a dihydrochloride, $C_{20}H_{36}Cl_2$, dechlorinated to a dicyclic hydrocarbon, $C_{20}H_{34}$. The ozonide of (I) affords CH_2O and HCO_2H and oxidation ($KMnO_4$) of (I) leads to a monocarboxylic acid, $C_{19}H_{32}O_3$, in which the oxide ring has remained intact. (I) is probably represented as shown. (II) is tricyclic; one O is ketonic and the other oxidic, and it differs only from (I) in the presence of CO which is adjacent to a CH_2. Dehydrogenation (Se) of the hydrocarbon obtained by treating (II) with HCl followed by NH_2Ph, gives some 1 : 3 : 5 : 6-$C_{10}H_4Me_4$. (III) contains 3 OH, one oxide ring, 3 carbocyclic rings, and one ethylenic linking.



(I.)



(II.)



(IV.)

II. One of the fractions from the neutral oil from *D. biforme* is manool, $C_{20}H_{34}O$, m.p. 56°, which forms a trihydrochloride, m.p. 119°, identical with that from (I). It is a dicyclic diterpene alcohol, with 2 double linkings and a C skeleton identical with that of (I). Tetrahydromanool (IV) is converted into a monohydrochloride, which loses HCl to give tetrahydromanoene, $C_{20}H_{36}$. The hydrocarbon on ozonolysis gives a mixture of a ketone, $C_{18}H_{32}O$ (semicarbazone, m.p. 202°), and a monobasic acid, $C_{16}H_{28}O_2$, m.p. 129°. F. R. S.

Behaviour of the apparent lignin during degradation of rye straw by hydrogen sulphite. R. S. Hilpert and A. Bolling (Ber., 1936, 69, [*B*], 1598—1601).—Treatment of rye straw with $Ca(HSO_3)_2$ followed by NaOH of NaOCl shows the lignin to consist of $\nless$ four chemically different components. About 67% of the lignin is dissolved by $Ca(HSO_3)_2$ whilst the remaining 33% is unattacked. One half of the residue is stable towards NaOCl and 33% is insol. in NaOH. If the residue from treatment with NaOH is subjected to treatment with NaOCl a pure white cellulose with 4% of lignin is obtained. The results cannot be harmonised with the hypothesis that lignin is a chemically defined component but are readily explained if it is regarded as a reaction product of sensitive substances, presumably carbohydrates. H. W.

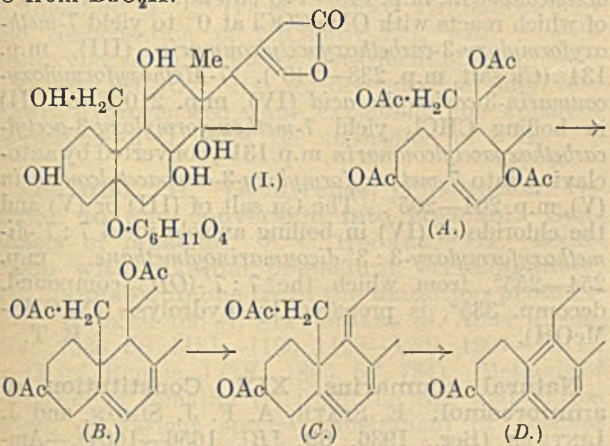
Highly polymerised compounds. CXLII. Lignin. H. Staudinger and E. Dreher (Ber., 1936, 69, [*B*], 1729—1737).—Determinations of the sp. viscosity of phenol-, acetylphenol-, *o*-cresol-, and *o*-acetylcresol-lignin in $COMe_2$, of beech-lignin in $COMe_2$ and HCO_2H, and of Na ligninsulphonate in HCO_2H show that lignin has a relatively low mol. wt. These and other properties prove that its structural principle differs from that of cellulose and similar highly polymerised compounds and that it is not formed of long chains. Conc. HCO_2H at 100° dissolves about 50% of the lignin of pine without addition of mineral acid; the product is a mixture of aromatic substances rich in OMe. Gradual addition of H_2O to its solution in dioxan ppts. fractions differing little in OMe content and having mol. wt. about 1000 in freezing dioxan. Their solutions in dioxan or HCO_2H are of low viscosity. The treatment of pine wood with HCO_2H produces also considerable amounts of sugar-like substances sol. in H_2O from the polysaccharides present. Cellulose is also attacked to some extent, but the products formed are exempt from OMe. Insol. lignin has not the same structural principle as cellulose. H. W.

Resin. IV. Sublimed *l*-abietic acid. D. Lipkin and W. A. La Lande, jun. (J. Amer. Chem. Soc., 1936, 58, 1310—1311).—Sublimation (method essentially that of B., 1934, 726) of *l*-abietic acid (I) gives an acid (II), m.p. 150°, $[\alpha]_D^{25}$ −35·1° in EtOH (cf. Steele, A., 1922, i, 739), which is unaffected by light and air in the solid state. In xylene, however, (I) and (II) absorb O_2 at the same rate (method: Dupont and Lévy, A., 1930, 86). H. B.

Biochemistry of micro-organisms. LI. Metabolic products of *Aspergillus terreus*, Thom. II. Two new chlorine-containing mould metabolic products, geodin and erdin. H. Raistrick and G. Smith (Biochem. J., 1936, 30, 1315—1322; cf. A., 1935, 662).—When a strain of *A. terreus*, Thom, was grown on a glucose–Czapek–Dox solution containing KCl as the sole source of Cl, the amount of Cl′ in solution diminished approx. at the same rate as the glucose. Final acidification with H_2SO_4 gave a heavy ppt. containing 50% of the Cl originally present, from which were isolated: *geodin*, $C_{17}H_{12}O_7Cl_2$, m.p. 235°, $[\alpha]_{5461}^{20}$ +179°, $[\alpha]_{5790}^{20}$ +149° (both in $CHCl_3$), dibasic (Na_2 salt, $[\alpha]_{5461}^{20}$ +72·4°), containing 2 OMe; giving with CH_2N_2 a *compound*, $C_{16}H_7O_4N_2Cl_2(OMe)_3$, m.p. 151°, $[\alpha]_{5461}^{22}$ −58° in C_6H_6: a H_2-derivative, m.p. 229°, optically inactive; and *erdin*, $C_{16}H_{10}O_7Cl_2+0{\cdot}5EtOH$, m.p. 211° (decomp.), optically inactive, dibasic, containing 1 OMe, giving with CH_2N_2 a *compound*, $C_{16}H_7O_4N_2Cl_2(OMe)_3$, m.p. 154°, not identical with the corresponding isomeric compound from geodin (H_2-derivative, $C_{16}H_{12}O_7Cl_2+0{\cdot}5H_2O$, m.p. 240°, giving on heating a cryst. sublimate). Substitution of KBr or KI for KCl in the medium did not affect growth but did not result in the isolation of brominated or iodinated metabolic products. P. W. C.

Ouabain. L. F. Fieser and M. S. Newman (J. Biol. Chem., 1936, 114, 705—710).—Ouabain is probably (I). The positions of the OH are determined by the course of acetolysis of hepta-acetyldeoxydihydro-ouabain and *iso*ouabain, indicated in the partial formulæ (*A*)—(*D*). Loss of the *tert*.-

$O\cdot C_6H_{11}O_4$ gives the grouping $C:C\cdot C\cdot OAc$; the next two ethylenic linkings arise by the tendency to form conjugated linkings coercing the activated OAc. Expulsion of $CH_2\cdot OAc$ (as CH_2O and Ac_2O) is caused by the tendency to form an aromatic ring. The aromatic nature of ring *B* is not precluded by its slow hydrogenation and is confirmed by the similarity of the absorption spectra of the trianhydrolactone (II) from *iso*ouabain, dihydrotrianhydrostrophanthidin, and neoergosterol. (II) slowly absorbs 1—1·8 O from BzO_2H.



R. S. C.

Crystalline substances from the adrenal gland. H. L. Mason, C. S. Myers, and E. C. Kendall (J. Biol. Chem., 1936, **114**, 613—631).—Repeated partition of the crude extract of minced adrenal glands between H_2O and C_6H_6 gives fractions, (I) more sol. in C_6H_6, (II) more sol. in H_2O, and (III) equally sol. in H_2O and C_6H_6, which are all mixtures. (I) yields *substances* (*A*), $C_{26}H_{36}O_5$, m.p. 177—179·5°, $[\alpha]_{5461}^{25}$ +347° in C_6H_6, and (*B*), $C_{24}H_{34(36)}O_5$, m.p. 135—139°. With $K_2Cr_2O_7$ (*A*) gives the unsaturated *acid*-1, $C_{20}H_{26}O_4$, decomp. 245—260°, $[\alpha]_{5461}^{25}$ +290° in 30% EtOH (contains 1 active H and 2 CO); crude (I) gives either this acid or the saturated *acid*-2, $C_{20}H_{28}O_4$, decomp. 240—260°, $[\alpha]_{5461}^{25}$ +267° in 30% EtOH. (*B*) may be the precursor of acid-2. Acids-1 and -2 resist CrO_3, but are oxidised by alkaline Ag_2O. (I) gives sub-fractions, (*a*), (*b*), and (*c*). (*a*) yields a *substance* (*C*), m.p. 220—227°, $[\alpha]_{5461}^{25}$ +110° in EtOH, +56° in C_6H_6, probably impure $C_{21}H_{34}O_5$ (contains 3 OH and 1 CO), which with alkaline Ag_2O gives 45% of a saturated *acid*-3, $C_{21}H_{34}O_6$, decomp. 240—242°, oxidised by $K_2Cr_2O_7$ to a *ketone*-1, $C_{20}H_{30}O_3$, m.p. 159—160° after sintering at 156°. Oxidation of (*b*) with Ag_2O gives an unattacked mixture, m.p. 142—145° (decomp.), 10—20% of acid-3, and a mixture of acids; of the last-mentioned mixture part readily gives a lactone, stable to CrO_3, and the remainder is oxidised by CrO_3 to *ketone*-2, $C_{19}H_{28}O_3$, m.p. 159—161° (*semicarbazone*, cryst.). (*a*) and (*b*) give acids with hot dil. NaOH; when the mixture (*c*) is thus treated, it gives a polyhydric *alcohol*, *substance* (*D*), $C_{20}H_{36}O_5$, m.p. 214—216° (usually softens at 170°), $[\alpha]_{5461}^{25}$ +29° in $COMe_2$, very hygroscopic, which with HCl–EtOH gives an unsaturated *substance*, $C_{20}H_{34}O_5$, +0·5H_2O, m.p. 150—155°, and with hot H_2SO_4–EtOH a *substance*, $C_{20}H_{34(36)}O_5$, +0·5H_2O, m.p. 172—178°. With CrO_3 (*D*) gives *ketone*-3, $C_{18}H_{24}O_3$, m.p. 160—161·5°, $[\alpha]_{5461}^{25}$ +229° in C_6H_6 [contains 1 OH and 1 CO; *oxime*, m.p. 205—232° (decomp.)]. (III) yields some (*D*) and *substance* (*E*), $C_{21}H_{30}O_5$, m.p. 201—208° (decomp.), $[\alpha]_{5461}^{25}$ +269° in C_6H_6 [absorption max. at 2370 A.; 2 : 4-*dinitrophenylhydrazone*, m.p. 255—256° (decomp.)]. Unsaturation is detected by $C(NO_2)_4$, OH and CO by MgMeI. (*C*) is probably $C_{19}H_{30}O(OH)_2{>}C(OH)\cdot CHO$, giving on oxidation $C_{19}H_{30}O(OH)_2{>}C(OH)\cdot CO_2H$ (acid-3) and then $C_{19}H_{30}O(OH)_2CO$ (ketone-1). R. S. C.

Lactone group of the cardiac aglucones and the Grignard reagent. W. A. Jacobs and R. C. Elderfield (J. Biol. Chem., 1936, **114**, 597—599).—As expected from the presence of an active H in the $\Delta^{\beta\gamma}$-lactone group, the dianhydrolactone (I) from strophanthidin with MgMeI gives 1 CH_4, digitoxigenin 3 and its acetate 2, but the H_4-derivative of (I) gives only 0·57 and the two anhydrodigitoxigenins only 1·4 mol. In general expectation is realised, but the exceptions in the lit. require explanation. R. S. C.

Action of mixed organo-magnesium compounds on the esters and *N*-disubstituted amides of α-phenyl-β-2-furylacrylic acid. N. Maxim and N. Stancovici (Bull. Soc. chim., 1936, 3, [v], 1319—1328; cf. A., 1934, 1360).—MgEtBr with α-phenyl-β-2-furylacryldiphenylamide (cf. A., 1935, 757) in boiling Et_2O affords α-*phenyl*-β-2-*furylvalerdiphenylamide*, b.p. 262°/11 mm., hydrolysed to α-phenyl-β-2-furylvaleric acid (I) (cf. A., 1935, 756). The following are prepared similarly: *diphenylamide*, b.p. 261°/10 mm., and *diethylamide*, b.p. 232°/14 mm., of αβ-diphenyl-β-2-furylpropionic acid (II); *diethylamide*, b.p. 223°/12 mm., of (I); *methylanilides*, b.p. 244°/12 mm. and 262°/13 mm., of (I) and (II), respectively. Similarly from the appropriate esters of α-phenyl-β-2-furylacrylic acid (III) with MgEtBr are obtained exclusively the Et, *Pr*, b.p. 170°/8 mm., *Bu*, b.p. 179°/10 mm., and *amyl* ester, b.p. 192°/7 mm., of (I). With MgPhBr, the appropriate esters of (III) afford the *Et*, b.p. 210°/8 mm., *Pr*, b.p. 226°/9 mm., *Bu*, b.p. 230°/9 mm., and *amyl* ester, b.p. 236°/9 mm., of (II), together with ααβ-*triphenyl*-γ-2-*furyl*-Δ^{β}-*propen*-α-*ol*, m.p. 174°. J. L. D.

Action of mixed organo-magnesium compounds on α-phenyl-β-2-furylacrylonitrile. II. N. Maxim and G. Aldea (Bull. Soc. chim., 1936, 3, [v], 1329—1334; cf. A., 1935, 756).—α-Phenyl-β-2-furylacrylic acid with MgMeI in boiling Et_2O affords α-*phenyl*-β-2-*furylbutyronitrile*, b.p. 167°/10 mm. (*acid*, b.p. 208°/18 mm.; acid *chloride*, b.p. 165°/12 mm.; *amide*, b.p. 221°/15 mm.; *Et* ester, b.p. 428°/15 mm.). The following are prepared similarly: αγ-*diphenyl*-β-2-*furylbutyronitrile*, b.p. 241°/18 mm. (*acid*, m.p. 118°; acid *chloride*, b.p. 184°/17 mm.; *amide*, m.p. 165°; *Et* ester, b.p. 230°/17 mm.); α-*phenyl*-β-2-*furyl*-ε-*methylheptonitrile*, b.p. 187°/13 mm. (*acid*, b.p. 215°/12 mm.; acid *chloride*, b.p. 187°/10 mm.; *amide*, m.p. 130°; *Et* ester, b.p. 192°/20 mm.); and α-*phenyl*-β-p-*tolyl*-β-2-*furylpropionitrile*, b.p. 219°/20 mm. (*acid*, m.p. 163°). J. L. D.

Condensation of benzoin and thymol. II. Constitution of nitration products of 2 : 3-

diphenyl-4-methyl-7-*iso*propylcoumarone. O. Dischendorfer and A. Verdino (Monatsh., 1936, **68**, 81—91).—2 : 3-Diphenyl-4-methyl-7-*iso*propylcoumarone (I) with HNO_3 in AcOH gives a *substance* which is the 6-*NO_2*-derivative (II), m.p. 151°, since it is oxidised (CrO_3) to 4-*nitro*-6-*benzoyloxy*-2-*methyl*-5-iso*propylbenzophenone*, m.p. 110°, which is hydrolysed to the 6-*OH*-compound [5-*nitro*-2-*benzoylthymol*], m.p. 130—131°, in which the NO_2 is shown to be in the thymol nucleus by $KMnO_4$ oxidation to BzOH. 3-*Nitro*-6-*hydroxy*-2-*methyl*-5-iso*propylbenzophenone* [4-*nitro*-2-*benzoylthymol*] (III), m.p. 124—125°, is prepared by nitration of 2-benzoylthymol (which with $KMnO_4$ also gives BzOH), and this structure for (II) thereby excluded. With $NHPh{\cdot}NH_2$ or $Na_2S_2O_4$, (II) yields the 6-*NH_2*-derivative of (I), m.p. 146°, of which the *Ac* derivative, m.p. 231°, is nitrated to 5-*nitro*-6-*acetamido*-2 : 3-*diphenyl*-4-*methyl*-7-iso*propylcoumarone*, m.p. 281°. A second nitration product of (I) is 5-*nitro*-2 : 3-*dihydroxy*-2 : 3-*diphenyl*-4-*methyl*-7-iso*propylcoumarone*, m.p. 160°, which is oxidised (CrO_3) to 3-*nitro*-6-*benzoyloxy*-2-*methyl*-5-iso*propylcoumarone* [4-*nitro*-2-*benzoylthymol benzoate*], m.p. 145°, which on hydrolysis yields (III). A third nitration product of (I) is also obtained, but not identified. E. W. W.

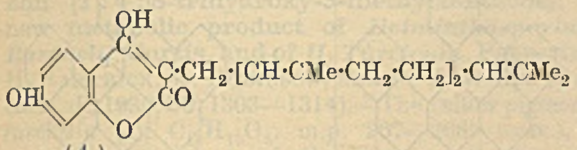
Synthesis of 3-hydroxy-2-ketocoumaran and *p*-hydroxymandelic acid. K. Ladenburg, K. Folkers, and R. T. Major (J. Amer. Chem. Soc., 1936, **58**, 1292—1294).—*o*-$OH{\cdot}C_6H_4{\cdot}CHO$ in 10% aq. $NaHSO_3$ with aq. $NaCN+Et_2O$ gives the unstable *o-hydroxymandelonitrile*, not distillable, converted by Et_2O–HCl into the imino-ether hydrochloride, which is hydrolysed to 3-*hydroxy*-2-*ketocoumaran* (I), m.p. 107—108°. (I) is partly hydrolysed in aq. solution to *o*-$OH{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CO_2H$ (*Ca* salt). *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ is similarly converted into *p*-$OH{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$, m.p. 99—102° (lit. 98°), and thence into *p*-$OH{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CO_2H$, m.p. 109·5—110·5° (lit. 105—108°) (*Et* ester, m.p. 128·5—129°). Introduction of *o*- or *p*-OH into $OH{\cdot}CHPh{\cdot}CO_2H$ does not increase the bactericidal activity towards *S. aureus* and *E. typhi*. H. B.

***iso*Flavone series.** P. C. Mitter and S. S. Maitra (J. Indian Chem. Soc., 1936, **13**, 236—259).—The *azlactone*, m.p. 168°, from β-resorcylaldehyde Me_2 ether with boiling 10% NaOH gives 2 : 4-*dimethoxyphenylpyruvic acid*, hygroscopic, m.p. 156°, the *oxime*, m.p. 145° (decomp.), of which with Ac_2O at 100° gives 2 : 4-*dimethoxyphenylacetonitrile*, m.p. 76°. This affords (Hoesch) 2 : 4 : 6-*trihydroxy*-2′ : 4′-*dimethoxyphenylacetophenone* (I), m.p. 175°, the *Ac_2* derivative, m.p. 204—205°, of which with hot 1% KOH–EtOH yields 5 : 7-*dihydroxy*-2′ : 4′-*dimethoxy*-2-*methyl*iso*flavone*, m.p. 213—214° (does not fluoresce in aq. alkali; pink colour with H_2SO_4, violet → brown with $FeCl_3$). The *$(CH_2Ph)_2$* derivative, m.p. 135°, of (I) does not condense with HCO_2Et and "mol." Na. R. S. C.

Synthesis of (A) di(coumarino-3-carboxyl)-methane (B) 7 : 7′-dihydroxydi(coumarino-3-carboxyl)methane. M. Trenknerówna (Rocz. Chem., 1936, **16**, 6—11, 12—18).—(A) The chloride of coumarin-3-carboxylic acid (I) and $CH_2Ac{\cdot}CO_2Et$ (II) in boiling $CHCl_3$ yield *Et coumarinyl*-3-*carboxylacetoacetate*, m.p. 125—126°, converted into 3-*acetoacetylcoumarin*, m.p. 143—144°, the Cu *salt*, m.p. 280°, of which condenses with (I) (in boiling anisole; 3 hr.) to yield di(coumarino-3-carboxyl)methane, also prepared in the same way from (I) and Et (coumarinyl-3-carboxyl)acetate, or from Et di(coumarinyl-3-carboxyl)acetate (in boiling anisole; 20 min.).

(B) 2 : 4-$(OH)_2C_6H_3{\cdot}CHO$ and $CO(CH_2{\cdot}CO_2Et)_2$, in presence of piperidine, afford 7-*hydroxy*-3-*carbethoxyacetylcoumarin*, m.p. 146—148°, an aq. NaOH solution of which reacts with $OMe{\cdot}COCl$ at 0° to yield 7-*methoxyformyloxy*-3-*carbethoxyacetylcoumarin* (III), m.p. 134° (*Cu* salt, m.p. 238—240°). 7-*Methoxyformyloxycoumarin*-3-*carboxylic acid* (IV), m.p. 210°, and (II) in boiling $CHCl_3$ yield 7-*methoxyformyloxy*-3-*acetylcarbethoxyacetylcoumarin*, m.p. 131°, converted by autoclaving into 7-*methoxyformyloxy*-3-*acetoacetylcoumarin* (V), m.p. 204—205°. The Cu salt of (III) or (V) and the chloride of (IV) in boiling anisole yield 7 : 7′-*dimethoxyformyloxy*-3 : 3′-*dicoumarinoylmethane*, m.p. 254—255°, from which the 7 : 7′-*$(OH)_2$*-compound, decomp. 335°, is prepared by hydrolysis (NaOMe–MeOH). R. T.

Natural coumarins. XIX. Constitution of ammoresinol. E. Späth, A. F. J. Simon, and J. Lintner (Ber., 1936, **69**, [*B*], 1656—1664).—Ammoniacum resin is shaken with Et_2O and the filtered solution is extracted with 5% Na_2CO_3. The extract is acidified with HCl, immediately extracted with Et_2O, and the residue left after removal of the solvent is converted by Ac_2O at 100° into diacetylammoresinol (I), b.p. 210—225° (bath)/0·02 mm., m.p. 101—102°. (I) is converted by cautious treatment with 2*N*-Na_2CO_3 in MeOH into *acetylammoresinol* (III), m.p. 128—129°, and by KOH–MeOH at 60° into ammoresinol (III), m.p. 107—108° (vac.). Analyses of (I), (II), and (III) confirm the formula $C_{24}H_{30}O_4$ for (III). Treatment of (III) with CH_2N_2 in MeOH–Et_2O gives *methylammoresinol* (IV), b.p. 220—235° (bath)/0·005 mm., difficultly sol. in cold, readily in hot, dil. aq. alkali indicating that 2 O of (III) are present in a lactone group. Styphnic and β-resorcylic acid are formed by the degradation of (I). Oxidation of (IV) with $KMnO_4$ yields 2-hydroxy-4-methoxy- and 2 : 4-dimethoxy-benzoic acid. Repetition of Caspari's work shows that the oxidation of (I) leads to 2-hydroxy-4-acetoxybenzoic acid [whence the 2 : 4-$(OMe)_2$-acid] and not γ-resorcylic acid, the residue of which is therefore not a component of (III). Catalytic hydrogenation (Pd–C in AcOH) of (I) affords diacetylhexahydroammoresinol, b.p. 210—220° (bath)/0·02 mm., m.p. 62—64°, oxidised by $KMnO_4$ in alkaline solution to δθμ-*trimethyltetradecoic acid* (V), b.p. 135—145°/0·03 mm. [p-*xenylamide*, m.p. 98—99° (vac.)]. The constitution of (V) is established by its formation by the oxidation of βξκ-trimethylpentadecan-ξ-one (VI) by Br in NaOH and by its conversion into (VI) by treatment with $SOCl_2$ followed by Zn–Cu, MeI, and EtOAc in C_6H_6. (III) therefore contains a single carbocyclic 6-membered ring. Further insight into the structure of the side-chain is afforded by the ozonolysis of (I) to β-methyl-Δ^{β}-hepten-ζ-one, indicating the presence of isoprene units. Distillation of (III) at 200—230°/0·3 mm. affords resacetophenone and 7-*hydroxy-3-methylbenzotetronic acid* (VII), m.p. 304—305°. (III)



(*A*.)

is therefore *A*. (VII) is obtained synthetically by the condensation of $CHMe(CO_2Et)_2$ with 2 : 4-diacetoxybenzoyl chloride and treatment of the product with 50% H_2SO_4. Its Ac_2 derivative is only very slowly hydrogenated, thus explaining the apparent saturation of (I) after the absorption of 3 H_2.

H. W.

Lomatiol. II. Occurrence, constitution, relation to and conversion into lapachol. Synthesis of lapachol. S. C. Hooker. **III. Oxidation with alkaline potassium permanganate. IV. Violet quinone from the oxidation product.** S. C. Hooker and A. Steyermark (J. Amer. Chem. Soc., 1936, **58**, 1181—1190, 1198—1201, 1207—1211).—II (cf. Rennie, J.C.S., 1895, **67**, 784). Methods of isolation of lomatiol (I) from the ripe and unripe fruits of various species (Australian) of *Lomatia* are given; (I) is absent from seeds of several species from Chile. (I) is now shown to be 3-*hydroxy*-2-δ-*hydroxy*-γ-*methyl*-Δ^{β}-*butenyl*-1 : 4-*naphthaquinone*. Reduction (H_2, PtO_2, EtOH) of (I) affords either (mainly) *hydrolomatiol* (the 2-δ-*hydroxy*-γ-*methylbutyl* derivative), m.p. 101—102° [converted by conc. H_2SO_4 into (VI) (below)], or hydrolapachol (the 2-*iso*amyl derivative), m.p. 93·5—94°, probably owing to variations in the catalyst. *iso*Lomatiol (II) (the 2-β-hydroxy-γ-methyl-Δ^{γ}-butenyl derivative) and hydroxy*iso*lapachol (J.C.S., 1896, **69**, 1355) are both similarly reduced to 3-*hydroxy*-2-β-*hydroxy*-iso*amyl*-1 : 4-*naphthaquinone* (=*hydro*iso*lomatiol*=β-*hydroxyhydrolapachol*) (III), m.p. 120·5—121·5°; (I) and (II) are not, therefore, stereoisomerides (cf. *loc. cit.*). (I) is converted by cold aq. H_2SO_4 into dehydro-*iso*-β-lapachone (5 : 6-*benzo*-1-iso*propenylcoumaran*-3 : 4-*quinone*) (IV), m.p. 116—116·5° [*quinoxaline*, m.p. 157·5—158°, from o-$C_6H_4(NH_2)_2$], hydrolysed (1% NaOH) to (II). (II) and dil. H_2SO_4 also give (IV); conc. H_2SO_4 affords hydroxy-β-lapachone (3-hydroxy-2 : 2-dimethyl-3 : 4-dihydro-αβ-naphthpyran-5 : 6-quinone), m.p. 203—205°. (IV) is reduced (H_2, PtO_2, EtOH–AcOH) to iso-β-*lapachone* (the 1-Pr^{β} derivative) (V), m.p. 124·5—125·5°, which could not be prepared by reduction of the corresponding coumarone (*loc. cit.*). (V) is hydrolysed (1% NaOH) to (III), which is converted by conc. H_2SO_4 into β-lapachone (VI). The above work also constitutes a synthesis of lapachol.

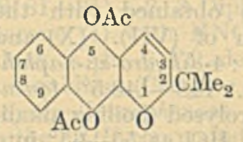
III. Lomatiol is oxidised (1% $KMnO_4$, 1% NaOH) to 3-*hydroxy*-2-γ-*hydroxy*-β-*methyl*-Δ^{α}-*propenyl*-1 : 4-*naphthaquinone* (VII) and a little 1-*methyl*-4 : 5-*benzocoumarone*-3 : 6-*quinone*, m.p. 246—247° (largely unaffected by dil. alkali). (VII) heated alone or with dil. HCl passes into the red 3-*methyl*-ββ-*naphthpyran*-5 : 10-*quinone* (VIII), m.p. 196·5—197·5°, reduced (Adams) to the 3 : 4-H_2-derivative (IX), m.p. 170·5—171°, which is hydrolysed (1% NaOH) to 3-*hydroxy*-2-γ-*hydroxy*iso*butyl*-1 : 4-*naphthaquinone* (X), m.p. 147·5—148·5°, also obtained with the 2-Bu^{β} derivative by reduction of (VII). (X) and conc. H_2SO_4 give 3-*methyl*-3 : 4-*dihydro*-αβ-*naphthpyran*-5 : 6-*quinone* (XI), m.p. 148—148·5° (*quinoxaline*, m.p. 163—163·5°), hydrolysed (boiling alkali) to (X) and converted by conc. HCl at 55—65° into (IX).

IV. Hydrolysis (1% NaOH) of (VIII) gives an unstable OH-compound which passes readily into the violet 3-*methyl*-αβ-*naphthpyran*-5 : 6-*quinone* (XII), m.p. 156—158° (decomp.) (*quinoxaline*, m.p. 163—163·5°); a little of a *compound*, m.p. 239—240° (decomp.), is also isolated. (XII) is converted into (VIII) by boiling EtOH, H_2O, or very dil. HCl; hydrolysis (conc. H_2SO_4 or, better, 0·25% NaOH in air) affords 3-*hydroxy*-2-β-*formyl*-Δ^{α}-*propenyl*-1 : 4-*naphthaquinone*, m.p. 229—230° (decomp.) [*Me*, 160—161°, *Et*, m.p. 184·5—185·5° (H_2-derivative, m.p. 185—186°), and Bu^{α}, m.p. 121·5—122°, *semiacetals*, formed by the action of AlkOH, which may be 2-alkoxy-3-methyl-ββ-naphthpyran-5 : 10-quinones], which is converted by aq. NH_3 into a *compound*, m.p. 136—137°, and by boiling AcOH into an *anhydride*, $C_{28}H_{18}O_7$, m.p. 243—244° (decomp.). (XII) is reduced (Adams) to (XI).

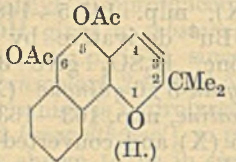
H. B.

Constitution of lapachol and its derivatives. IV. Oxidation with potassium permanganate. V. Structure of Paternò's "*iso*lapachone." S. C. Hooker (J. Amer. Chem. Soc., 1936, **58**, 1168—1173, 1190—1197).—IV. Oxidation (1% $KMnO_4$) of lapachol (3-hydroxy-2-γ-methyl-Δ^{β}-butenyl-1 : 4-naphthaquinone) in 1% NaOH at about 0° gives 3-*hydroxy*-2-β-*methyl*-Δ^{α}-*propenyl*-1 : 4-*naphthaquinone* (I), m.p. 119—120° [*acetate*, m.p. 85·5—86°; *compound*, $C_{20}H_{16}ON_2$, m.p. 226—227° (decomp.), with o-$C_6H_4(NH_2)_2$], which is further oxidised to 2-hydroxy-1 : 4-naphthaquinone and is reduced (H_2, PtO_2, EtOH) to 3-*hydroxy*-2-iso*butyl*-1 : 4-*naphthaquinone* (II), m.p. 132·5—133·5°. Similar oxidation of hydrolapachol affords (II), whilst hydroxyhydrolapachol (J.C.S., 1892, **61**, 611; 1896, **69**, 1356) yields 3-*hydroxy*-2-β-*hydroxy*iso*butyl*-1 : 4-*naphthaquinone* (III), m.p. 121—122°. 3-*Hydroxy*-2-sec.-*butyl*-1 : 4-*naphthaquinone*, m.p. 92·5—93°, is obtained by reduction of the 2-α-methylallyl derivative (Fieser, A., 1927, 462). (I) and (III) are converted by short treatment with cold conc. H_2SO_4 into 5 : 6-*benzo*-1 : 1-*dimethylcoumaran*-3 : 4-*quinone*, m.p. 187—188° [*quinoxaline*, m.p. 154—155°, from o-$C_6H_4(NH_2)_2$], which is hydrolysed (1% NaOH) to (III), is converted by aq. HCl at 50—65° into 3-*hydroxy*-2-β-*chloro*iso*butyl*-1 : 4-*naphthaquinone*, m.p. 147—148° (decomp.), and is isomerised by HBr (*d* 1·49) at 65—69° to 4 : 5-*benzo*-1 : 1-*dimethylcoumaran*-3 : 6-*quinone*, m.p. 183—184° [also obtained from (III) and boiling dil. HCl or H_2SO_4], also hydrolysed (1% NaOH) to (III). Lapachol and 3-hydroxy-2-*n*-amyl-1 : 4-naphthaquinone with PbO_2 in AcOH give *peroxides*, m.p. 154—155° and 117—118°, respectively.

V. Acetylation (Ac_2O–NaOAc) of lapachol affords 5 : 10-*diacetoxy*-2 : 2-*dimethyl*-ββ-*naphthpyran* (I), m.p. 131—132° [identical with the Ac_2 derivative described

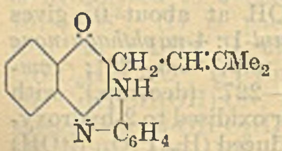


(I.)



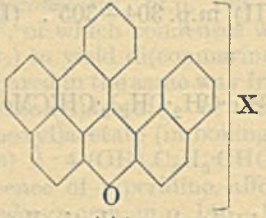
(II.)

by Paternò (A., 1883, 210)], and 5 : 6-*diacetoxy-2 : 2-dimethyl-αβ-naphthpyran* (II), m.p. 128—129°, which give different colours with conc. H_2SO_4. Successive reduction (H_2, PtO_2, EtOH) [whereby the 3 : 4-H_2-derivatives, m.p. 169·8—170° and 162—162·6°, respectively (cf. Monti, A., 1915, i, 824), are produced] and hydrolysis (AcOH–H_2SO_4 in air) of (I) and (II) gives α-lapachone (2 : 2-dimethyl-3 : 4-dihydro-ββ-naphthpyran-5 : 10-quinone) (III) and β-lapachone (2 : 2-dimethyl-3 : 4-dihydro-αβ-naphthpyran-5 : 6-quinone) (IV), respectively. Hydrolysis (AcOH–dil. H_2SO_4, aq. NaOH, or EtOH–KOH in air) of both (I) and (II) affords *dehydrolapachone* (most probably 2 : 2-*dimethyl*-ββ-*naphthpyran*-5 : 10-*quinone*) (V), m.p. 142·5—143°, reduced (Adams) to (III) and converted by Zn–Ac_2O into (I). Paternò's *iso*lapachone (*loc. cit.*) is (V). Reductive acetylation of "*iso*propylfurano-1 : 2- and -1 : 4-naphthaquinones" (J.C.S., 1896, 69, 1355), which are isomeric with (V), gives the corresponding *quinol diacetates*, m.p. 135·5—136·5° and 167—168°, respectively. The above formulation of (V) as a 1 : 4-quinone is uncertain in view of the following results. *o*-$C_6H_4(NH_2)_2$ and (V) in AcOH yield *dehydrolapazine* (VI), m.p. 156·5—157°, which is formulated as the quinoxaline from 2 : 2-dimethyl-αβ-naphthpyran-5 : 6-quinone; lapachol similarly furnishes *lapeurhodone* (VII), m.p. 161·5—162·5°, which is oxidised (air in aq. NaOH+Et_2O) to (VI). Reduction (Adams) of (VI) gives *lapazine*, two forms, m.p. 130·5—131·5° and 121·5—122·5°, also obtained from (VII) and cold conc. H_2SO_4 and from (IV) and *o*-$C_6H_4(NH_2)_2$. Methyllapeurhodone [from lapachol and *o*-tolylenediamine (VIII)] is oxidised [as (VII)] to *methyldehydrolapazine*, two forms, m.p. 149—151·5° and 169·5—171·5°, also formed from (V) and (VIII). Bromo-β-lapachone [the 3-Br-derivative of (IV)] (J.C.S., 1892, **61**, 611) is hydrolysed by 1% NaOH at room temp. to dihydroxyhydrolapachol (IX) (*loc. cit.*) and a little (V); 5% NaOH affords (IX) and 3-hydroxy-2-β-methyl-Δ^a-propenyl-1 : 4-naphthaquinone, m.p. 119—120° [also obtained from (V) and 10% NaOH alone or in presence of Zn dust (with subsequent atm. oxidation)]. Acetylation (Ac_2O–NaOAc) of 3-hydroxy-2-allyl-1 : 4-naphthaquinone gives a *diacetate*, $C_{17}H_{14}O_5$, m.p. 178·5—179·5°, in addition to that [new m.p. 223·5—224·5° (decomp.)] described by Fieser (A., 1927, 155). H. B.

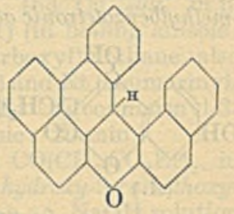


(VII.)

Pyrenium compounds. XXV. Dehydrenium dyes ; new class of carbenium salts. W. Dilthey and F. Quint [in part with R. Knipp] (Ber., 1936, **69**, [*B*], 1575—1591).—Treatment of *ms*-phenyldibenzoxanthanol with $AlCl_3$ at 175—200° affords *dehydro*-ms-*phenyldibenzoxanthenium chloride* (I) (*A*; X=Cl) (corresponding *picrate* and *perchlorate*). The one-sided ring-closure is established by analysis of the salts and by the similarity of the reaction with the corresponding *o*-tolyl compounds (see below). With carbinols the change is effected with certainty by $AlCl_3$, but with the salts irradiation or treatment with $ZnCl_2$ is requisite. Thus *ms*-phenyldibenzoxanthenium perchlorate and $ZnCl_2$ at 400—500° yield (I), whence the corresponding *bromide* (X=Br+0·5HBr) and *iodide*, $C_{27}H_{16}OI_2$. Reduction of (I) by Zn dust in boiling AcOH affords *dehydro*-ms-*phenyldibenzoxanthane* (*B*), m.p. 250—252° (decomp.), immediately re-oxidised to *A* by PbO_2 in AcOH. *ms-o*-Chlorophenyldibenzoxanthanol and $AlCl_3$ eliminate HCl with production of (I). *p*-C_6H_4Me·CHO and β-$C_{10}H_7$·OH in AcOH–12*N*-HCl at 100° afford ms-p-*tolyldibenzoxanthane*, m.p. 228—229°, oxidised by PbO_2 in AcOH to ms-p-*tolyldibenzoxanthanol*, m.p. 265—266° (decomp.) after softening at 255°. Treatment of this with $AlCl_3$ at 200° or exposure of its *perchlorate*, m.p. 286—287°, in AcOH to sunlight leads to *dehydro*-ms-p-*tolyldibenzoxanthenium chloride* (corresponding *picrate*), reduced to *dehydro*-ms-p-*tolyldibenzoxanthane*, m.p. 229—230° (decomp.) after softening. *o*-C_6H_4Me·COCl, (β-$C_{10}H_7)_2O$, and $AlCl_3$ at 120—150° give ms-o-*tolyldibenzoxanthanol*, decomp. 245—246° after softening, transformed by $AlCl_3$ into *dehydro*-ms-o-*tolyldibenzoxanthenium chloride*, which could not be reduced to a cryst. xanthane. *Dehydro*-ms-o-*tolyldibenzoxanthenium perchlorate* is obtained by irradiation of ms-o-*tolyldibenzoxanthenium perchlorate*, m.p. 293—294° (decomp.) after softening. Irradiation of *ms*-o-chlorophenyldibenzoxanthenium perchlorate is accompanied by loss of HCl. Dehydrogenation of *ms-o*-chlorophenyldibenzoxanthane cannot be effected with $AlCl_3$ and only with difficulty by irradiation in AcOH in presence of O_2 which can be replaced by methylene-blue or *p*-benzoquinone. *p*-C_6H_4Cl·COCl, (β-$C_{10}H_7)_2O$, and $AlCl_3$ in CS_2 yield p-*chlorophenyldibenzoxanthanol* (III), m.p. 275—276° (decomp.) after softening (*perchlorate*, m.p. 291°): it is transformed by $AlCl_3$ into (I). *Dehydro*-ms-p-*chlorophenyldibenzoxanthenium perchlorate* is obtained slowly by exposure to sunlight and O_2 of a solution of *ms-p*-chlorophenyldibenzoxanthenium perchlorate in boiling AcOH whereas the corresponding *picrate* is obtained similarly from (III) and picric acid in the same solvent. β-$C_{10}H_7$·OH and β-$C_{10}H_7$·CHO in HBr–AcOH give ms-1′-*naphthyldibenzoxanthane*, m.p. 245° and, after re-solidification, m.p. 253—254·5°, oxidised by PbO_2 in boiling AcOH to ms-1-*naphthyldibenzoxanthanol*, decomp. 280—281° when placed in bath preheated to 270°. 1′-*Naphthyldibenzoxanthenium perchlorate*, m.p. 325° (decomp.) after softening at 315°, is dehydrogenated in sunlight by



(*A*.)



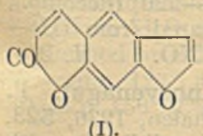
(*B*.)

O_2 in boiling AcOH to *dehydro*-ms-1′-*naphthyldibenzoxanthenium perchlorate.* H. W.

Biochemistry of micro-organisms. L. Ravenelin (1 : 4 : 8-trihydroxy-3-methylxanthone), a new metabolic product of *Helminthosporium Ravenelii*, Curtis, and of *H. Turcicum*, Passerini. H. Raistrick, R. Robinson, and D. E. White (Biochem. J., 1936, **30**, 1303—1314).—The yellow pigment, *ravenelin* (I), $C_{14}H_{10}O_5$, m.p. 267—268° (corr.), a metabolism product of the plant pathogens *H. Ravenelii*, Curtis, and *H. Turcicum*, Passerini, is optically inactive, has pseudo-acidic characters, contains 1 side-chain Me as shown by the Roth–Kuhn micro-method, gives an O-*triacetate*, m.p. 204—205°, (corr.), O-*tribenzoate*, m.p. 255° (corr.), O-*trianisoyl* derivative, m.p. 216—218° (corr.), a *Br*$_3$-derivative, resorcinol by KOH fusion, a *Me*$_2$ *ether*, m.p. 285—287° (corr.), and a *Me*$_3$ *ether* (II), m.p. 178—179°. (II) was inert to alkalis and Ac_2O, was basic, and gave a *ferrichloride*, $C_{17}H_{17}O_5FeCl_4$, m.p. 174—175° (corr.), with HNO_3 gave a *nitrodimethylravenelin*, m.p. 224—226°, with MgPhBr gave the *Et ether* of *phenyltrimethoxyxanthydrol*, m.p. 166°, and with $NaNH_2$ gave an oil identical with synthetic 2 : 5 : 3′-*trimethoxy*-3-*methyldiphenyl ether* since both gave the same *Br*$_4$-derivative, m.p. 152°. The above facts limit the structure to 1 : 4 : 8-(or 1 : 4 : 6-)trihydroxy-3-methylxanthone. The synthesis of 1 : 4 : 6-*trimethoxy*-3-*methylxanthone*, m.p. 157°, is described and as this is not identical with (II), (I) must be 1 : 4 : 8-*trihydroxy*-3-*methylxanthone*. The following compounds were synthesised in the preps. above : 4-*bromo*-2 : 5-*dimethoxytoluene*, m.p. 90—91° (corr.); 2 : 5 : 3′-*trimethoxy*-4-*methyldiphenyl ether*, b.p. 192—195°/2·5 mm., m.p. 72—74° (corr.) (*Br*$_3$-derivative, m.p. 130°); 2 : 5 : 3′-*trimethoxy*-3-*methyldiphenyl ether*, b.p. 165—166°/0·5 mm. [*Br*$_3$-derivative, m.p. 133° (corr.)]; 4 : 5 : 3′-*trimethoxy*-2-*methyldiphenyl ether*, b.p. 160—162°/0·2 mm., m.p. 68—69° (corr.) (*Br*$_4$-derivative, m.p. 115°). The optimum cultural conditions for the production of (I) by *H. Ravenelii* were determined and the relationship of (I) to the polyhydroxyanthraquinones also produced by *Helminthosporia* is discussed. Only two other naturally occurring hydroxyxanthones—euxanthone and gentisin—have been previously isolated. P. W. C.

Colouring matter of the flowers of *Lantana camera*, Linn.—See this vol., 1166.

Components of leaves of *Ficus carica*. K. Okahara (Bull. Chem. Soc. Japan, 1936, **11**, 389—394).—The aq. extract of the leaves yields crystals of *ficusin* (I), $C_{11}H_6O_3$, m.p. 161—162°, which is sol. in warm alkali and contains a lactone ring, the third O being inert. Catalytic reduction affords *tetrahydroficusin*, $C_{11}H_{10}O_3$, m.p. 154°, methylation *methylficusinic acid*, $OMe{\cdot}C_{10}H_6{\cdot}CO_2H$, m.p. 161·5—162°, and nitration in AcOH *nitroficusin*, $C_{11}H_5O_3{\cdot}NO_2$, m.p. 254°. Oxidation of (I) with H_2O_2 in alkaline solution yields furan-2 : 3-dicarboxylic acid and alkali fusion 4 : 6-dimethoxy*iso*phthalic acid. (I) is therefore as shown. The $COMe_2$ extract of the leaves contained bergapten which with Me_2SO_4 and alkali gave *methylbergaptenic acid*, $C_{14}H_{12}O_6$, m.p. 138°. A. T.



(I).

Arsenic and iodine compounds of the pyridine series. A. Binz and H. Maier-Bode (Angew. Chem., 1936, **49**, 486—489; cf. A., 1935, 1156).—Details are given of the prep. of the As compounds described previously. 3-Iodo-2-hydroxypyridine and 3-iodo-2-pyridone-*N*-acetic acid have been prepared by diazotisation of 3-amino-2- and -4-hydroxypyridine, respectively. 5-*Bromo*-3-*amino*-4-*hydroxypyridine* has been prepared by reduction of 5-bromo-3-nitro-4-hydroxypyridine. Action of I in KI on 3-hydroxypyridine in the cold yields 2-*iodo*-3-*hydroxypyridine*, and warm yields (? 2 : 5-)*di-iodo*-3-*hydroxypyridine*. The stability of I-compounds of C_5H_5N, as examined by heating under pressure with H_2O at 170°, decomp. with HNO_3, and pptg. with $AgNO_3$, is $\gg$ that of the C_6H_6 series, thus explaining why Selectan compounds can pass into the organism by intravenous application without eliminating I, and so can be used as harmless *X*-ray contrast media. J. W. S.

Reduction products of nicotinamide methiodide. P. Karrer, G. Schwarzenbach, F. Benz, and U. Solmssen (Helv. Chim. Acta, 1936, **19**, 811—828).—Nicotinamide [from Et nicotinate (I) and NH_3–MeOH at 150°], m.p. 151° (*methochloride*, m.p. about 240°), gives a *methiodide*, m.p. 204°, which with $Na_2S_2O_4$ yields a yellow, oily 1-*methyldihydronicotinamide* (II), which resembles Warburg's co-enzyme in that it is a very powerful reducing agent [cold $AgNO_3$ instantaneously, methylene-blue, indigotin-di-, -tri-, and -tetra-sulphonate; can be titrated potentiometrically with $K_3Fe(CN)_6$], gives a very high negative potential to Pt, and has an absorption band at 360 mμ, changed to 295—300 mμ by acid (which also causes much loss of reducing power). On these accounts and because it has no blue fluorescence (II) is a 1 : 2- or 1 : 6-H_2-derivative. Acidification gives a colourless, cryst. *isomeride*, decomp. about 236° (darkening from 200°), which has an intense blue fluorescence, reduces $AgNO_3$ only when heated, is stable to $K_3Fe(CN)_6$, and is thus the 1 : 4-H_2-compound. 1-Methyl-2- or -6-butyl-1 : 2- or -1 : 6-dihydronicotine and *NN*′-dibenzyltetrahydrodipyrydyl, but no 1 : 4-H_2-compounds, can be titrated with $K_3Fe(CN)_6$. *Nicotinmethylamide* [from (I)], m.p. 102°, ω-*ethoxynicotinimide dihydrochloride* (III) (from nicotinonitrile and HCl–EtOH), m.p. about 233°, *nicotinmethylamidine dihydrochloride* [from (III) and NH_2Me], m.p. about 240°, nicotinamide methoxymethochloride, and pyridine glucosidobromide do not give similar H_2-compounds. R. S. C.

Synthesis of *dl*-proline from pyrrole. F. K. Signaigo and H. Adkins (J. Amer. Chem. Soc., 1936, **58**, 1122—1124).—Alternate addition (in portions) of 1 mol. each of $ClCO_2Et$ and MgEtBr to pyrrole+MgEtBr (1 : 1) followed by a further mol. of $ClCO_2Et$ gives Et pyrrole-1- (26·4) and -2-carboxylate (1·5), and -1 : 2-dicarboxylate (65%). The last is reduced (method: this vol., 861) to Et pyrrolidine-1 : 2-dicarboxylate, hydrolysed (conc. HCl) to *dl*-proline (over-all yield 57%). H. B.

Pyrrole series. I. Preparation of *N*-methylpyrroles. A. H. Corwin and W. M. Quattle-

BAUM, jun.

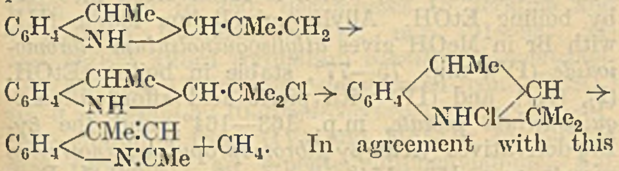
II. Mechanism of aldehyde synthesis of pyrromethenes. A. H. CORWIN and J. S. ANDREWS (J. Amer. Chem. Soc., 1936, 58, 1081—1085, 1086—1090).—I. The question of *N*-isomerism (*i.e.*, position of NH groups in porphin nucleus) is discussed briefly (cf. Fischer and Loy, A., 1923, i, 718; Conant and Bailey, A., 1933, 403). Et 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate (I) (improved prep.) with Na in PhMe followed by Me_2SO_4 gives the 1 : 2 : 4-*Me*$_3$ ester (II), m.p. 113—114°, converted by SO_2Cl_2 in AcOH at 60° into *Et 2-formyl*-1 : 4-*dimethylpyrrole*-3 : 5-*dicarboxylate*, m.p. 94°, also prepared by methylation (Me_2SO_4, MeOH–KOH) of (VI) (below). (II) is hydrolysed (conc. H_2SO_4 at <30°) to the 5-*Et* 3-*H* ester, decomp. 192°, decarboxylated in glycerol to *Et* 1 : 2 : 4-*trimethylpyrrole*-5-*carboxylate*, m.p. 47°, the 3-*Ac* derivative (III), m.p. 62°, of which, best prepared by methylation [as for (I)] of the 3-acetyl-2 : 4-dimethyl derivative, is reduced (method: Fischer *et al.*, A., 1929, 1463) to 1 : 2 : 4-*trimethyl*-3-*ethylpyrrole* (IV), b.p. 93°/23 mm. (IV) and 40% CH_2O in 95% EtOH give (provided mineral acid is absent) 1 : 3 : 5 : 1′ : 3′ : 5′-*hexamethyl*-4 : 4′-*diethyl*-2 : 2′-*dipyrrylmethane* (V), m.p. 106°, which could not be oxidised to a methene. (IV) and (V) are both oxidised (aq. CrO_3, 20% H_2SO_4) to the *N*-Me derivative, b.p. 215—220°, of methylethylmaleimide. Reduction [H_2 (2500 lb.), Raney Ni, EtOH, 150°] of (III) affords *Et* 1 : 2 : 4-*trimethyl*-3-*ethylpyrrole*-5-*carboxylate*, b.p. 124°/2 mm., also obtained by methylation (Me_2SO_4, *tert.*-amyl alcoholic Na *tert.*-amyloxide) of the 2 : 4-Me_2 ester. Et 2-formyl-4-methylpyrrole-3 : 5-dicarboxylate (VI) and Et 2 : 4-dimethylpyrrole-3-carboxylate with dry HCl in Et_2O (other methods unsuccessful) give 3 : 5 : 4′-*tricarbethoxy*-4 : 3′ : 5′-*trimethylpyrromethene hydrochloride*, sinters >120°, decomposed by boiling EtOH to (VI) and unidentified material. Hydrolysis (EtOH–KOH) of (II) yields the 3-*Et* 5-*H* ester, decarboxylated to *Et* 1 : 2 : 4-*trimethylpyrrole*-3-*carboxylate*, m.p. 62°, which with 40% CH_2O and EtOH–HCl affords 4 : 4′-*dicarbethoxy*-1 : 3 : 5 : 1′ : 3′ : 5′-*hexamethyl*-2 : 2′-*dipyrrylmethane*, m.p. 151—152°, which could not be oxidised (Br) to the methene. Attempts to prepare 1-methyl- and 1 : 1-dimethyl-pyrromethenes from some of the above *N*-Me derivatives were unsuccessful. 4 : 4′-Dicarbethoxy-3 : 5 : 3′ : 5′-tetramethylpyrromethene (VII) could not be methylated [as for (I)]; decomp. occurs.

II. The (anomalous) production of (VII) from Et 2 : 4-dimethylpyrrole-3-carboxylate (VIII) and Et 2-formyl-4-methyl-3-ethylpyrrole-5-carboxylate (Fischer and Ernst, A., 1926, 621) is best explained by the intermediate formation (and subsequent fission) of a tripyrrylmethane (*A*). It is now shown that (*A*) can be intermediates in the Piloty synthesis of pyrromethenes. 4 : 4′ : 4″-Tricarbethoxy-3 : 5 : 3′ : 5′ : 3″ : 5″-hexamethyltri-2-pyrrylmethane, new m.p. 220—225° (decomp.) (sinters at 195°) (prep. Fischer and Heyse, A., 1925, i, 76), with Et 5-formyl-2 : 4-dimethylpyrrole-3-carboxylate (IX) (improved prep.) in aq. MeOH–HBr give the hydrobromide of 4 : 4′-dicarbethoxy-3 : 5 : 3′ : 5′-tetramethylpyrromethene (X) [best identified by reduction (H_2, PtO_2, EtOH) to the methane, m.p. 230°], also obtained similarly from (IX) and (VIII). *Et* 5-*formyl*-1 : 2 : 4-*trimethylpyrrole*-3-*carboxylate* (XI), m.p. 97° [from (IX) and Na_2O in C_6H_6 followed by Me_2SO_4], with (VIII) (2 mols.) and dry HCl in C_6H_{14} affords (X) (as hydrochloride) and Et 1 : 2 : 4-trimethylpyrrole-3-carboxylate (XII); with equimol. quantities, (X), (XI), and (XII) are isolated. 4 : 4′ : 4″-*Tricarbethoxy*-1 : 3 : 5 : 3′ : 5′ : 3″ : 5″-*heptamethyltri*-2-*pyrrylmethane*, m.p. 177° (prep. as *loc. cit.*), is also cleaved by aq. MeOH–HBr to (X). Short treatment of (IX) and (XII) with aq. MeOH–HBr gives 4 : 4′ : 4″-*tricarbethoxy*-1 : 3 : 5 : 1′ : 3′ : 5′ : 3″ : 5″-*octamethyltri*-2-*pyrrylmethane*, m.p. 147—148° [also prepared from (IX), (XII), and $KHSO_4$ at $\ngtr 150$°], which is then cleaved to (X). (X) is also formed (cf. Fischer and Zerweck, A., 1922, i, 758; 1923, i, 364) from (IX) and aq. MeOH–HBr, but in presence of (XII) reaction occurs at a lower temp. and gives a better yield. Cryst. compounds could not be obtained from (XI) and (XII). H. B.

Oxindole-amines from isatin. W. R. CONN and H. G. LINDWALL (J. Amer. Chem. Soc., 1936, 58, 1236—1239; cf. A., 1935, 501).—Isatin and $MeNO_2$ in EtOH–$NHEt_2$ give 3-*hydroxy*-3-*nitromethyloxindole* (I), m.p. 135—140° (decomp. to original components); $EtNO_2$ similarly affords 3-*hydroxy*-3-α-*nitroethyloxindole*, m.p. 145—150° (red at 140°). 5-*Bromo*-3-*hydroxy*-1-*ethyl*-, m.p. 123—125° (decomp.), and 3-*hydroxy*-1-*methyl*-, m.p. 98—99° (decomp.), and -1-*ethyl*-, m.p. 84—85° (decomp.), -3-*nitromethyloxindoles* are obtained from the appropriate *N*-alkylisatin. These NO_2-compounds gradually decompose into the original components when heated in neutral solvents; decomp. is retarded by a little AcOH and accelerated by inorg. or org. bases. Benzoylformanilide, $MeNO_2$, and EtOH–$NHEt_2$ afford α-*hydroxy*-α-*nitromethylphenylacetanilide*, m.p. 143—144° (decomp.), reduced (Sn, conc. HCl) to a compound, m.p. 208—210°. Reduction (H_2, PtO_2, AcOH) of (I) gives 3-hydroxy-3-aminomethyloxindole (II) [*hydrochloride*, m.p. 195—197° (decomp.); *picrate*, m.p. 165—166° (decomp.); N-*Bz* derivative, m.p. 177°], which with MeI in EtOH+$Ba(OH)_2$ affords 3-*hydroxy*-1-*methyl*-3-*oxindolylmethyltrimethylammonium iodide*, m.p. 227° (decomp.). Reduction of (I) with mossy Sn and conc. HCl also gives (II), but in one case some 3-hydroxy-3-hydroxylaminomethyloxindole (*hydrochloride*, m.p. 194°; *picrate*, m.p. 174°) was also produced. 5-Bromo-3-hydroxy-1-ethyl-3-aminomethyloxindole (III) [*hydrochloride*, m.p. 192—194° (decomp.); *picrate*, m.p. 182—183°; ON-*Bz*$_2$ derivative, m.p. 204°] and 3-hydroxy-1-ethyl-3-aminomethyloxindole (IV) [*hydrochloride*, m.p. 180—182° (decomp.); *picrate*, m.p. 168—169°; ON-*Bz*$_2$ derivative, m.p. 191° (decomp.); N-*CO*$_2$*Et* derivative, m.p. 166°] are also obtained by reduction with Sn and HCl. 3-*Hydroxy*-, m.p. 208—209° (decomp.), 3-*hydroxy*-1-*ethyl*-, m.p. 216—217° (decomp.), and 5-*bromo*-3-*hydroxy*-1-*ethyl*-, m.p. 218—220° (decomp.), -3-*carbamidomethyloxindole* are prepared from (II)—(IV) (as hydrochlorides) and aq. KCNO. H. B.

Supposed "acetoneanil" of Knoevenagel. P. KALNIN [with W. GRINSTEIN] (Annalen, 1936, 523, 118—129).—Oxidation of "acetoneanil" (I) with $KMnO_4$ gives AcOH in large amount and a *substance*

$C_{38}H_{39}O_3N_3$, m.p. (indef.) 142—190°. The observations are not in harmony with Reddelien's formulation of (I), which appears to be 3-*methyl*-2-iso*propenylindoline* (II), passing into 2 : 4-dimethylquinoline (III) not by simple elimination of CH_4 but by a complex mol. transformation,



$$C_6H_4{<}\begin{matrix}CHMe\\NH\end{matrix}{>}CH\cdot CMe{:}CH_2 \rightarrow$$

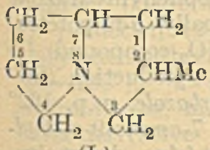
$$C_6H_4{<}\begin{matrix}CHMe\\NH\end{matrix}{>}CH\cdot CMe_2Cl \rightarrow C_6H_4{<}\begin{matrix}CHMe\\NHCl\end{matrix}{>}\begin{matrix}CH\\CMe_2\end{matrix} \rightarrow$$

$$C_6H_4{<}\begin{matrix}CMe{:}CH\\N{:}CMe\end{matrix} + CH_4.$$

In agreement with this hypothesis, a yellow intermediate *product* has been isolated which has the same composition as (II) and passes into (III) when treated with dry HCl. A mode of passage of $CMe_2{:}NPh$ into (II) is given. The methiodide, m.p. 251—252°, of (III) is converted by MgMeI in Et_2O into 1 : 2 : 2 : 4-*tetramethyl*-1 : 2-*dihydroquinoline*, m.p. 157—158° (corr.), the odour of which resembles that of (I) and which yields a picrate, m.p. 147°, identical with that of (I). Since (I) is not a dihydroquinoline derivative, a mol. rearrangement must occur either during the methylation of (I) or during the formation of the picrate.

H. W.

Syntheses of a new heterocyclic type formed from two condensed pyrrolidine rings. G. Menschikov (Ber., 1936, **69**, [*B*], 1802—1804).—2-*iso*Butylpyrrolidine is treated with Br in 5% NaOH at −5° and the oily bromoamine is treated with conc. H_2SO_4 thus giving 2-*methylpyrrolizidine* (I), b.p. 162—163°/atm. pressure (*picrate*, m.p. 182—184°), which does not decolorise $KMnO_4$ in 10% H_2SO_4 and is inert towards HNO_2. The corresponding *methiodide*, m.p. 225—226°, passes when treated with Ag_2O and then heated into *de*-N-*methyl*-2-*methylpyrrolizidine*, b.p. 164—166°/atm. pressure, hydrogenated (PtO_2 in 1% HCl) to *dihydrode*-N-*methyl*-2-*methylpyrrolizidine* (II), b.p. 165—167°/atm. pressure (*picrate*, m.p. 174—175°), which does not reduce acid $KMnO_4$. Since (II) is not identical with 1-methyl-2-*iso*butylpyrrolidine it is probably 1 : 4-dimethyl-2-*n*-propylpyrrolidine. Since (II) is not identical with the corresponding degradation product of heliotridane, the latter is certainly not (I). H. W.



(I.)

Benzoylation of quinoline oxide. M. Henze (Ber., 1936, **69**, [*B*], 1566—1568).—Quinoline oxide forms a *picrate*, $(C_9H_7ON)_2,C_6H_3O_7N_3$, m.p. 158°, which passes into the normal picrate, m.p. 143°, when treated with excess of picric acid. The corresponding hydrochloride is converted by BzCl and NaOH into 2-hydroxyquinoline [*picrate*, m.p. 132°; *hydrochloride* ($+1H_2O$), m.p. 192° (decomp.)]. Addition of BzCl to 2-methylquinoline oxide hydrochloride and excess of KCN in H_2O affords 2-*cyanoquinoline*, m.p. 93°, transformed by cold, conc. HCl into the corresponding *amide*, m.p. 123°, and by the boiling reagent into the acid, m.p. 156° [*Cu* ($+2H_2O$) salt]. H. W.

Derivatives of 8-hydroxyquinoline. E. Moness and W. G. Christiansen (J. Amer. Pharm. Assoc., 1936, **25**, 501—504).—2-*Amino*-p-*propylphenol*, m.p. 140—142° (from 2-*nitro*-p-*propylphenol*, b.p. 110°/4 mm.), by the Skraup reaction affords 8-*hydroxy*-5-*propylquinoline*, m.p. 52—52·5° (explosive; characterised by the 7-*Cl*-derivative [*hydrochloride*, m.p. 242° (decomp.)]). 5-Chloro-8-hydroxyquinoline in $PhNO_2$ with Me_2SO_4 affords a mixture of the methochloride and -sulphate. 8-*Dimethylaminoethoxyquinoline dihydrochloride* is prepared from 8-hydroxyquinoline (Na salt) and $NEt_2\cdot C_2H_4Br,HBr$ in EtOH whilst 5-amino-8-hydroxyquinoline refluxed with $NEt_2\cdot C_2H_4Cl$ in C_6H_6 gives 5-(β-*diethylaminoethylamino*)-8-*hydroxyquinoline dihydrochloride*. The Skraup reaction with Me 3-amino-4-ethoxybenzoate affords 8-ethoxyquinoline-5-carboxylic acid [*diethylaminoethyl* ester (impure), m.p. 86°]. 5-Chloro- and 5-nitro-8-hydroxyquinoline with $Hg(OAc)_2$ in aq. EtOH afford the corresponding *anhydro-mercuric* derivatives. None of the above compounds possesses significant trypanocidal or anæsthetic activity.

F. O. H.

Optically active silver–hydroxyquinoline complexes. F. Hein and H. Regler (Ber., 1936, **69**, [*B*], 1692—1702; cf. A., 1935, 868).—Treatment of 8-hydroxyquinoline with $AgNO_3$ in EtOH or C_5H_5N gives *Ag di-8-hydroxyquinoline nitrate*, $[Ag(C_9H_6N\cdot OH)_2]NO_3$, converted by NH_3 into the corresponding *base*, $OAg\cdot C_9H_6N,OH\cdot C_9H_6N$, and by C_5H_5N into the *compound*, $[Ag(C_9H_6N\cdot OH)_2],C_5H_5N$. The base is transformed by the requisite acid into the *trichloroacetate*, d-*mandelate*, and d-*camphorsulphonate*. Fractional treatment of it with α-bromo-*d*-camphor-π-sulphonic acid gives salts with extreme vals. of $[\alpha]^{19}_{D}$ +37·4°±0·5° and +47·8°±0·5°, thus establishing the existence of salts of differing optical activity and probably of the tetrahedral configuration of the complex. Attempts to obtain an optically active base from the salt fractions were unsuccessful.

H. W.

5 : 7-Di-iodo-8-hydroxyquinoline. V. Papesch and R. R. Burtner (J. Amer. Chem. Soc., 1936, **58**, 1314).—8-Hydroxyquinoline in 15% HCl added slowly to ICl in 15% HCl at room temp. gives 83·5—92·5% of nearly pure 5 : 7-I_2-derivative. H. B.

Preparation of 8-aminoquinoline from 8-chloroquinoline. N. N. Voroshcov, jun., and S. P. Mitzengendler (J. Gen. Chem. Russ., 1936, **6**, 681—684).—8-Chloroquinoline (I) and aq. NH_3 (20 mols.) in presence of CuCl (200°/49—55 atm.; 2·5 hr.) give 8-aminoquinoline in 69·3% yield. (I) undergoes partial decomp. to quinoline hydrochloride during distillation. R. T.

Organic nitrogen bases from pyrolysis of cotton-seed meal. I. Parker, C. L. Gutzeit, A. C. Bratton, and J. R. Bailey (J. Amer. Chem. Soc., 1936, **58**, 1097—1104).—The bases formed by pyrolysis of the meal consist of light petroleum-sol. (*A*) and -insol. (*B*) substances. The higher fractions of (*B*) have abnormally high N contents and tend to decompose to tars. The following are isolated from the lower fractions of (*A*): C_5H_5N; 2-, 3-, and 4-methyl-, 3-ethyl-, 2 : 4-, 2 : 6-, and 3 : 5- [picrate, m.p. 242·5—243·5° (lit. 228—230° and 244°)] -dimethyl-, and 2 : 4 : 6-trimethyl-pyridine; quinoline; *iso*-

quinoline; 2- and 4-methyl- and 2 : 3 : 8-trimethylquinoline; a *base*, $C_{11}H_{14}N_2$, b.p. 283°/750 mm. [*picrate*, m.p. 261—263° (decomp.) (darkens at 259°); *hydrochloride mercurichloride*, m.p. 173—174° (sinters at 150°)], which is probably a dihydroquinazoline. H. B.

Quinoline derivatives. IV. K. S. Narang, J. N. Ray, and T. D. Sachdeva (J. Indian Chem. Soc., 1936, **13**, 260—263).—The azlactone from veratraldehyde with hot 3% KOH gives α-*benzamido*-3 : 4-*dimethoxycinnamic acid*, m.p. 208°, reduced by 2·5% Na–Hg to α-*benzamido*-β-3 : 4-*dimethoxyphenylpropionic acid*, m.p. 158°, which with HNO_3–H_2SO_4–AcOH at 50° affords the 6-NO_2-*acid*, m.p. 208°; by reduction [$Fe(OH)_2$] and spontaneous ring-closure this yields 3-*benzamido*-2-*keto*-6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 225°. Piperonal leads similarly to α-*benzamido*-3 : 4-*methylenedioxycinnamic acid*, m.p. 224°, α-*benzamido*-β-3 : 4-*methylenedioxypropionic acid* (I), m.p. 122°, its 6-NO_2-derivative (II), m.p. 210°, and 3-*benzamido*-2-*keto*-6 : 7-*methylenedioxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 254°. Hydrolysis of (I) gives 3 : 4-*methylenedioxyphenylalanine dihydrochloride*, $+H_2O$, m.p. 278—280°. Reduction [$Fe(OH)_2$] of the *anilide*, m.p. 205°, of 6-nitro-3 : 4-methylenedioxycinnamic acid (III) does not give an amidine, but affords by hydrolysis 6 : 7-*methylenedioxy*-2-*quinolone*, m.p. 205°, also obtained by direct reduction of (III). Similarly, reduction of (II) or of N-β-6-*nitro*-3 : 4-*methylenedioxyphenylpropionylanthranilic acid* [from the acid chloride of (II) and $NH_2·C_6H_4·CO_2H$ in C_5H_5N], m.p. 208°, affords 2-*keto*-3 : 4-*methylenedioxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m.p. 232°. R. S. C.

Quaternary derivatives of heterocyclic compounds.—See B., 1936, 716.

3 : 4 : 6-Triaminoquinolines.—See B., 1936, 716.

Synthesis of derivatives of 3-methyl*iso*quinoline. V. Bruckner and A. Krámli (J. pr. Chem., 1936, [ii], **145**, 291—300).—The large-scale prep. of *iso*safrole ψ-nitrosite (78% yield) and thence of β-nitro-α-3 : 4-methylenedioxyphenyl-*n*-propyl acetate (68%) is described. β-Acetamido-α-3 : 4-methylenedioxyphenyl-*n*-propyl alcohol, prepared therefrom by reduction, is hydrolysed by hot 10% H_2SO_4 and the base converted without isolation into other acylamino-derivatives. With $POCl_3$ in PhMe or xylene at 110—120° these give *iso*quinoline derivatives, the aralkoyl more readily than the aroyl compounds. The following are described: β-*Phenylacetyl*-, m.p. 136—138°, -*homopiperonoyl*-, m.p. 152—153°, -*homoveratroyl*-, m.p. 139°, -*benzoyl*-, m.p. 135°, and *piperonoyl*-α-3 : 4-*methylenedioxyphenyl*-n-*propyl alcohol*, m.p. 159°. 6 : 7-*Methylenedioxy*-1-*benzyl*-, m.p. 119° [*hydrochloride*, m.p. 264° (decomp.)], -piperonyl-, -veratryl-, m.p. 133° (lit. 125°) [hydrochloride, m.p. 219° (lit. 225°)], -phenyl-, and -3′ : 4′-methylenedioxyphenyl-3-*methyl*isoquin*oline* (I). (I) is accompanied by a *substance*, $C_{18}H_{15}O_5N$, m.p. 107—108°. R. S. C.

Homoneurine series. I. Bromo-derivatives of *iso*quinolinehomoneurine. C. Candea, E. Macovski, and J. Kühn (Bull. Soc. chim., 1936, [v], 3, 1309—1318).—Allyl*iso*quinolinium bromide (I) with 2 Br in MeOH affords βγ-*dibromopropyl*iso*quinolinium bromide* (II), m.p. 190—192° [corresponding *iodide*, m.p. 145—146° (decomp.)], but with excess of Br affords a Br_5-*derivative*, m.p. 86—87°, with 3 ionisable Br, which is reconverted into (II) by boiling EtOH. Allyl*iso*quinolinium iodide (III) with Br in MeOH gives *allyl*iso*quinolinium dibromoiodide* (IV), m.p. 75—77°, stable in boiling EtOH. (I), (III), and (IV) with picric acid afford *allyl*iso*quinolinium picrate*, m.p. 163—164°, and the βγ-Br_2-derivatives yield βγ-*dibromopropyl*iso*quinolinium picrate*, m.p. 153—154°. J. L. D.

Synthesis of *iso*quinoline derivatives. W. Krabbe (Ber., 1936, 69, [*B*], 1569—1572).—$OH·CPh_2·CH_2·NHBz$ is converted by MgPhBr in Et_2O and finally at 200—205° into *benz*-ββ-*diphenylvinylamide*, m.p. 132—134°, converted by P_2O_5 in boiling PhMe into 1 : 4-*diphenyl*iso*quinoline* (I), m.p. 132·5° (*picrate*, m.p. 152°). Similarly benz-ββ-diphenylethylamide affords 1 : 4-*diphenyl*-3 : 4-*dihydro*iso*quinoline*, m.p. 122°, dehydrogenated (Pd-sponge at 230—240°) to (I). H. W.

Structural problems in the indole group. 5- and 7-Nitrotetrahydrocarbazoles. S. G. P. Plant (J.C.S., 1936, 899—902).—Reduction (Sn–HCl; 15 hr.) of 8-chloro-5-nitrotetrahydrocarbazole yields 5-*amino-tetra*-, m.p. 183° (*Ac* derivative, m.p. 198°), and -*hexa-hydrocarbazole* (Ac_2 derivative, m.p. 264°; *Bz* derivative, m.p. 245°). Elimination of NH_3 from *cyclo*hexanone-*m*-nitrophenylhydrazone [aq. H_2SO_4 (1 : 9)] affords principally 5-nitrotetrahydrocarbazole and not the 7-NO_2-compound (I) (cf. Borsche *et al.*, A., 1908, 367). Reduction (Sn–HCl) of 7-*nitro*-9-*methyltetrahydrocarbazole*, m.p. 162° [from $MeSO_4$ and (I)], affords 7-*amino*-9-*methylhexahydrocarbazole*, m.p. 87—89° (Ac_2 derivative, m.p. 106°), identical with that obtained by electrolytic reduction of the 7-NO_2-compound. Chlorination of the Bz_2 derivative, m.p. 199°, of 7-aminohexahydrocarbazole yields 6-*chloro*-7-*benzamido*-9-*benzoylhexahydrocarbazole*, m.p. 182°. F. N. W.

Manufacture of condensation products containing sulphur and organic sulphur compounds.—See B., 1936, 686.

Preparation of dihydroacridines by the Grignard reaction. W. L. Semon and D. Craig (J. Amer. Chem. Soc., 1936, **58**, 1278—1282).—It is now shown (cf. A., 1935, 482) that *o*-$NHPh·C_6H_4·CO_2Me$ (I) and MgMeI give *o*-$NHPh·C_6H_4Bu^γ$ and 5 : 5-*dimethyl*-5 : 10-*dihydroacridine* (II), m.p. 125—126° [*Ac*, m.p. 153—154°, *Bz*, m.p. 294—297°, and N-*Ph*, m.p. 123°, derivatives; 1 : 1 *compounds*, m.p. 135—136° and 124°, with acridine and 5-methylacridine (III), respectively]; (II) is probably formed by dehydration of the intermediate *o*-$NHPh·C_6H_4·CMe_2·OH$. (II) is also obtained from (III) or acridone (IV) and MgMeI in $Bu^α{}_2O$. (II) heated with $NaNH_2$ gives the *N*-Na derivative (V), which with MeI in PhMe affords 5 : 5 : 10-*trimethyl*-5 : 10-*dihydroacridine*, m.p. 100—102°; the compound described by Stevens *et al.* (A., 1931, 1404) is a mixture of this and 5 : 10-*dimethyl*-5 : 10-*dihydro*-

acridine (VI), m.p. 140—141°. (V) heated further with (II) gives (III), which is also formed from (II) (0·3 mol.), $NHPh_2$ (0·45 mol.), and HCl (0·15 mol.) at 250°. Acridine methiodide and MgMeI yield (VI) and 10 : 10′-*dimethyl*-5 : 10 : 5′ : 10′-*tetrahydro*-5 : 5′-*diacridyl*, m.p. about 280° (decomp.), which when heated to 350° decomposes to acridine and 10-*methyl*-5 : 10-*dihydroacridine*, m.p. 91—93°. (I) and MgEtI afford (probably) o-*anilinophenyldiethylcarbinol*, b.p. 175°/2 mm., dehydrated (conc. H_2SO_4) to 5 : 5-*diethyl*-5 : 10-*dihydroacridine*, m.p. 90—91° [also obtained from (IV) and MgEtBr in $Bu^a{}_2O$], and (probably) an *o*-pentenyldiphenylamine, b.p. 150—155°/2 mm. 5 : 5-*Di*-n-*butyl*-5 : 10-*dihydroacridine*, m.p. 87—88°, is prepared from (IV) and $MgBu^aBr$. H. B.

Phenanthrene series. X. Naphthquinolines. E. MOSETTIG and J. W. KRUEGER (J. Amer. Chem. Soc., 1936, **58**, 1311—1312).—3-Aminophenanthrene {N-*Me*, m.p. 69—70° (all m.p. are corr.) [*hydrochloride*, m.p. 190—200° (decomp.)], and NN-Me_2 derivative, m.p. 75—76° [*hydrochloride*, m.p. 210—213° (decomp.)], formed by methylation (Me_2SO_4, aq. KOH) and separated by Hinsberg's method}, glycerol, H_3BO_3, $PhNO_2$, $FeSO_4$, and conc. H_2SO_4 give a *naphthquinoline*, m.p. 106—107° (*hydrochloride*, m.p. 239—243°), reduced (H_2, Cu chromite, EtOH, 135°) to a H_4-derivative, m.p. 72—74° (*hydrochloride*, m.p. 255—260°), which is further reduced (H_2, PtO_2, AcOH) to an H_8-derivative, m.p. 111—112° (*hydrochloride*, m.p. 305—307°). 3-α-Aminoethylphenanthrene (*hydrochloride*, m.p. 265—266°) is prepared by reduction (2·5% Na–Hg, EtOH–AcOH) of 3-acetylphenanthrene oxime (the 2-*isomeride* has m.p. 196—198°). 2 - α - Chloro - γ - dimethylaminopropyl - [*hydrochloride*, m.p. 248—252° (decomp.)] (from the α-OH-derivative and PCl_5 in $CHCl_3$) is reduced (H_2, Pd–$CaCO_3$, EtOH) to 2-γ-dimethylaminopropylphenanthrene (*hydrochloride*, m.p. 222—227°).
H. B.

Condensation of esters of unsaturated acids with carbamide. III. Z. JERZMANOWSKA-SIENKIEWICZOWA (Rocz. Chem., 1936, **16**, 172—180).—Et_4 ethylenetetracarboxylate, $CO(NH_2)_2$, and NaOEt in EtOH, at the b.p., yield Et_3 *hydantoinoethanetricarboxylate*, m.p. 132—133°, which condenses with a further mol. of $CO(NH_2)_2$, and eliminates $CH_2(CO_2Et)_2$, to yield *spiro*hydantoin. R. T.

Preparation of pyridinium iodides.—See B., 1936, 687.

Synthesis of 1-phenyl-2-methyl-4-ethyl-5-pyrazolone. Y. F. CHI and M. C. H. YANG (J. Amer. Chem. Soc., 1936, **58**, 1152—1153).—*Et formylbutyrate* (I), b.p. 37—38°/2 mm. (*semicarbazone*, m.p. 108—108·5°), obtained by acidification (AcOH) of the Na salt (A., 1935, 358), and the appropriate $NHAr{\cdot}NH_2$ give 1-*phenyl*- (II), m.p. 99—99·5°, 1-p-*nitrophenyl*-, m.p. 212—214° (slight decomp.), and 1-p-*bromophenyl*-, m.p. 170—171°, -4-*ethyl*-5-*pyrazolone*. (II) is methylated (MeOH–MeI at 100—110°) to the 2-*Me* derivative, m.p. 121—121·5°. (I) and aq. NH_2OH afford 4-*ethyl*-5-iso*oxazolone*, b.p. 113—114°/2 mm. H. B.

Sodium 1-phenyl-2 : 3-dimethylpyrazolonyl-4-aminomethylene sulphoxylate and dimethylpyrazolonyldiphenyl. 4 : 4′-Di-(1-phenyl-3-methyl)pyrazolonyl.—See B., 1936, 762.

Glyoxaline series. R. WEIDENHAGEN and R. HERRMANN [with H. WEGNER, and (FRL.) D. WISCHNEVSKY, E. SEURIG, and G. RADNIK] (Z. Wirts. Zuckerind., 1935, **85**, 762—778).—4-Nitro-5-methylglyoxaline and $SnCl_2$ give a 67% yield of 4-amino-5-methylglyoxaline [not isolated free; *dihydrochloride*, m.p. 186° (decomp.); picrate, m.p. 193°; :CHPh, m.p. 216°, *Ac*, m.p. 216°, *Bz*, m.p. 262°, Bz_2, m.p. 176°, and *phenylcarbamide* derivative, m.p. 283°]. 4-Nitroglyoxaline gives similarly a 20% yield of NH_2-derivative. Glyoxalines are obtained, usually in good yield, from ammoniacal CuO (1 mol.) and α-OH-aldehydes or α-acetoxyaldehydes, which are readily oxidised to αβ-diketones; some α-chloroketones, *e.g.*, $CH_2Cl{\cdot}COMe$, are sufficiently reactive to give glyoxalines in one step; others can be used by preliminary hydrolysis without isolation of the OH-ketone. Thus are obtained glyoxaline and the following derivatives: 4-Ph; 4-phenyl-2-methyl, m.p. 161—162° (lit. 158—159°); 4-*phenyl*-2-*ethyl*, m.p. 133°, and -2-iso*propyl*, m.p. 180°; 2 : 4-Ph_2, m.p. 193° (hydrochloride, $+H_2O$, m.p. 273°); 4-o-$OH{\cdot}C_6H_4$, m.p. 181°, 4-4′-*hydroxy*-m-*tolyl*, m.p. 136—137°, 4-p-*anisyl*, m.p. 136—137°, 4-p-$NHAc{\cdot}C_6H_4$, m.p. 250—251°, 4-p-$NH_2{\cdot}C_6H_4$, $+0{\cdot}5H_2O$ and $+H_2O$, m.p. 97°, 4-p-$CO_2H{\cdot}C_6H_4$, m.p. 308° (*hydrochloride*, $+H_2O$, m.p. 338°), 4-Me, 2 : 4-Me_2 (from acetoxy- or chloro-acetone), and 4-$OH{\cdot}CH_2$ [from $CO(CH_2{\cdot}OH)$], m.p. 93—94°, derivatives. ω-Chloro-*o*-hydroxyacetophenone and hot H_2O give much coumaranone and 20% of oω-*dihydroxyacetophenone*, m.p. 65°. ω - Chloro - 2 - hydroxy - 5 - methylacetophenone gives similarly 40% of oω-*dihydroxy*-5-*methylacetophenone*, m.p. 76—77°. R. S. C.

Thiobarbiturates. II. E. MILLER, J. C. MUNCH, F. S. CROSSLEY, and W. H. HARTUNG (J. Amer. Chem. Soc., 1936, **58**, 1090—1091).—The following 5 : 5-*dialkyl*-2-*thiobarbituric acids* are prepared from $CS(NH_2)_2$ and $CAlkAlk'(CO_2Et)_2$ in EtOH–NaOEt: 5-*ethyl*-5-n-*propyl*-, m.p. 174·5°, and -5-iso*butyl*-, m.p. 170·5°; 5-n-*propyl*-5-iso*propyl*-, m.p. 168·5°, -5-*allyl*-, m.p. 138°, -5-n-, -iso-, and -sec.-*butyl*, m.p. 135·5°, 132°, and 165°, respectively, and -5-n-*hexyl*-, m.p. 114·4°; 5-iso*propyl*-5-*allyl*-, m.p. 176·5°, -5-iso*butyl*-, m.p. 115—117°, and -5-n-*amyl*-, m.p. 98·5°; 5-n-*amyl*-, m.p. 112·5°, and 5-n-, m.p. 120—121°, and -iso-, m.p. 147°, -*butyl*-5-*allyl*-. H. B.

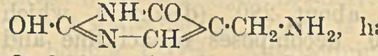
N-Arylbarbituric acids. J. S. BUCK (J. Amer. Chem. Soc., 1936, **58**, 1284—1286).—The following are prepared from $NH_2{\cdot}CO{\cdot}NHAr$ and $CEt_2(CO_2Et)_2$ or $CEtBu^a(CO_2Et)_2$ in EtOH–NaOEt: 1-phenyl-, m.p. 178°, 1-*p*-tolyl-, m.p. 155·5° (lit. 152—153°), 1-o-, m.p. 182°, and -m-, m.p. 133°, -*tolyl*-, 1-o-, m.p. 176·5°, and -m-, m.p. 115—116°, -*anisyl*-, 1-*p*-anisyl-, m.p. 129° (lit. 126—127°), 1-o-, m.p. 159°, and -m-, m.p. 114°, -*phenetyl*-, 1-*p*-phenetyl-, m.p. 160° (lit. 152—153°), and 1-α-, m.p. 207°, and -β-, m.p. 146°, -*naphthyl*-5 : 5-*diethylbarbituric acids*; 1-phenyl-, b.p. 203°/0·5 mm., m.p. about 70°, 1-o-, m.p. 135°, -m-, b.p. 212°/0·6 mm., m.p. about 89°, and -p-, m.p.

142°, *-tolyl-*, 1-o-, m.p. 139·5°, -m-, m.p. 102·5°, and -p-, m.p. 124°, *-anisyl-*, 1-o-, m.p. 131°, -m-, b.p. 216°/0·5 mm., m.p. 84—85°, and -p-, m.p. 100°, *-phenetyl-*, and 1-α-, m.p. 182°, and -β-, m.p. 126°, *-naphthyl-5-ethyl-5-*n*-butylbarbituric acids.* H. B.

Condensations of cyanoacetic esters with carbamide by magnesium methoxide. H. Lund (Ber., 1936, **69**, [*B*], 1621—1627).—$Mg(OMe)_2$ is a less powerful catalyst than NaOMe for the condensation of cyanoacetic esters with $CO(NH_2)_2$ to cyanoacetylcarbamides and thence to 4-imidobarbituric acids. Reaction usually ceases at the conclusion of the first phase and is accompanied by the formation of much by-product. $CN{\cdot}CH_2{\cdot}CO_2Et$, $Mg(OMe)_2$, and $CO(NH_2)_2$ afford $CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ in moderate yield when reaction is curtailed and 4-imidobarbituric acid when the change is prolonged. $CN{\cdot}CHPr^{\beta}{\cdot}CO_2Et$ gives 4-*imido*iso*propylbarbituric acid*, whence iso*propylbarbituric acid*, m.p. 216°. The prep. of 4-imidoethylbarbituric acid is described. Et *cyclo*hexenylcyanoacetate (I) appears to be transformed by $Mg(OMe)_2$ or NaOEt in *Et* cyclo*hexylidenecyanoacetate*, m.p. 274—275° (decomp.). Et benzylidenecyanoacetate gives *benzylidenecyanoacetylcarbamide*, m.p. 220° (decomp.), but no benzylidenebarbituric acid, which is obtained in 75% yield from $CHPh{:}CH(CO_2Et)_2$. 4-*Imidodiallylbarbituric acid*, decomp. 280—284°, whence diallylbarbituric acid, is derived from $(CHMe{:}CH_2)_2C(CN){\cdot}CO_2Et$, whereas $(CH_2Ph)_2C(CN){\cdot}CO_2Et$ yields *dibenzylcyanoacetylcarbamide*, m.p. 188°. *Et* cyclo*hexenylethylcyanoacetate* (II), b.p. 150—151°/15 mm., gives under varied conditions 4-*imido*cyclo*hexenylethylbarbituric acid*, decomp. about 265°, cyclo*hexenylethylcyano-acetylcarbamide*, m.p. 161°, and *-acetamide*, m.p. 103°. (I) and guanidine afford cyclo*hexylidenecyanoacetylguanidine*, whilst (II) yields cyclo*hexenylethylcyanoacetylguanidine*, m.p. 256—258° (decomp.). H. W.

4-*N*-Piperazylbenzenesulphonic acid. V. Prelog (Coll. Czech. Chem. Comm., 1936, **8**, 288—290).—Sulphonation of *N*-phenylpiperazine gives 1-*phenylpiperazine*-p-*sulphonic acid* (*Na* salt; *hydrochloride*; *Bz* derivative). F. R. S.

Reactions of aryl alkyl ketones with thiocarbamide. K. Dziewonski, K. Bernakiewicz, and L. Gizler (Bull. Acad. Polonaise, 1935, **A**, 564—571).—$CS(NH_2)_2$ and COPhMe at 170° give 4 : 6-*diphenyl*-6-*methyl*-1 : 2 : 3 : 6-*tetrahydro-2-thiopyrimidine* (I), m.p. 172—174° (*acetate*, m.p. 140°; *Ag* salt, m.p. 190—195°; Bz_2 derivative, m.p. 152—153°). (I) is transformed by MeI–MeOH at 100° into 2-*methylthiol*-4 : 6-*diphenyl*-6-*methyl*-5 : 6-*dihydropyrimidine*, m.p. 82—84° (*hydriodide*, m.p. 88—90°; *picrate*, m.p. 165—167°), and by EtOH–conc. HCl into 2-*ethylthiol*-4 : 6-*diphenyl*-6-*methyl*-3 : 6-*dihydropyrimidine hydrochloride*, m.p. 206—208° (decomp.). (I) and HgO in boiling AcOH afford 2-*keto*-4 : 6-*diphenyl*-6-*methyl*-1 : 2 : 3 : 6-*tetrahydropyrimidine*, m.p. 179—181°. Similarly $CS(NH_2)_2$ and $COMe{\cdot}C_6H_4Me$-*p* give 4 : 6-*di*-p-*tolyl*-6-*methyl*-1 : 2 : 3 : 6-*tetrahydropyrimidine*, m.p. 170—171° (*Ag* salt, m.p. 193—194°; *acetate*, m.p. 129—130°; *methiodide*, m.p. 188—189°), transformed by BzCl and Na_2CO_3 in boiling Et_2O into 2-*benzoylthiol*-4 : 6-*di*-p-*tolyl*-6-*methyl*-5 : 6-*dihydropyrimidine*, m.p. 152—153°. H. W.

Pyrimidines. CLIII. Structure of vitamin-B_1. T. B. Johnson and A. Litzinger (Science, 1936, **84**, 25—26).—*Thyminylamine*,  $OH{\cdot}C{<}\begin{smallmatrix}NH{\cdot}CO\\ N{-}CH\end{smallmatrix}{>}C{\cdot}CH_2{\cdot}NH_2$, has been synthesised. On heating, it gives uracil, CH_2O, and NH_3. L. S. T.

Pyrimidines. Synthesis of 4-methyl-5-*n*-butylcytosine. Y. F. Chi (J. Amer. Chem. Soc., 1936, **58**, 1150—1151).—$CHAcBu^{a}{\cdot}CO_2Et$ and $CS(NH_2)_2$ in EtOH–NaOEt give 6-*hydroxy*-4-*methyl*-5-n-*butyl*-2-*thiopyrimidine* (I), m.p. 197—198°, which with EtBr, MeI, and $CH_2Cl{\cdot}CO_2Et$ in EtOH–NaOEt affords 6-*hydroxy*-2-*ethylthiol*- (II), m.p. 92—93°, -2-*methylthiol*-, m.p. 158—159°, and -2-*carbethoxymethylthiol*-, m.p. 110—111° (and thence -2-*carboxymethylthiol*-, m.p. 117—118°), -4-*methyl*-5-n-*butylpyrimidine*, respectively. (II) is hydrolysed (conc. HBr) to 4-*methyl*-5-n-*butyluracil*, m.p. 245°, also obtained from (I) and aq. $CH_2Cl{\cdot}CO_2H$. 6-*Chloro*-2-*ethylthiol*-4-*methyl*-5-n-*butylpyrimidine*, b.p. 160°/2 mm. [from (II) and $POCl_3$ at 110—120°], with EtOH–NH_3 at 170—180° gives the 6-NH_2-derivative, m.p. 104—105°, hydrolysed (48% HBr) to 4-*methyl*-5-n-*butylcytosine* (+0·75H_2O), m.p. 299—300° (decomp.) [*hydrobromide*, m.p. 222° (decomp.); *hydrochloride*, m.p. 235°]. H. B.

Quinazolines. IV. S. S. Bedi and K. S. Narang (J. Indian Chem. Soc., 1936, **13**, 252—254).—Veratraldehyde is quantitatively nitrated at 5—10°. 6-Nitropiperonal and $KMnO_4$ at 40—60° give 6-nitropiperonylic acid, m.p. 175°, the *amide*, m.p. 191—193°, of which is reduced ($SnCl_2$) to the NH_2-*amide*, m.p. 172—174°; the *Ac* derivative, m.p. 212°, thereof in 1% NaOH at 40—50° gives 6 : 7-*methylenedioxy-2-methyl-4-quinazolone*, m.p. 346°. 6-β-*Carboxypropionyl*-, m.p. 219°, and 6-*butyrylaminopiperonylamide*, m.p. 271°, and 6 : 7-*methylenedioxy-2-β-carboxyethyl*-, m.p. 184°, and -2-n-*propyl*-4-*quinazolone*, m.p. 280°, are similarly prepared. R. S. C.

Heteropolar compounds. I. Complex halogenomercuric salts of 4-hydroxy-2-thion-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline. C. V. Gheorghiu and (Mlle.) L. Manolescu (Bull. Soc. chim., 1936, [v], **3**, 1353—1368; cf. A., 1934, 1011; 1935, 630, 1253).—2-Thion-4-ethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline (I) with $HgCl_2$ in EtOH affords a yellow *compound*, m.p. 119—121°, and the Hg^{II} *chloride*, m.p. 121—126°, of (I), an internal salt, which with hot xylene or with HCl in Ac_2O (through the intermediate red carbonium compound) affords the $HgCl_2$ internal salt of 2-thion-1 : 4-anhydro-3-phenyl-2 : 3-dihydroquinazoline (II), m.p. 290—292°. Similarly, (I) with $HgBr_2$ affords a *compound*, m.p. 138—144° (decomp.), and a colourless Hg^{II} *bromide*, m.p. 116—121°, which when heated with xylene or EtOBz affords the Hg^{II} *bromide* (III) of (II), m.p. 276°, which with cold Ac_2O containing HCl affords *mercurybis-(2-thiol-4-hydroxy-3-phenyl-3 : 4-dihydroquinazoline) dihydrochloride* (red), m.p. 230—232°. With HgI_2, (I) affords a similar series of *compounds*, m.p. 126—128°, 137—138° (decomp.) (IV) (converted into the former in hot EtOH), and 252—253°, respectively, which with HCl in Ac_2O affords a red carbonium *chloride*, m.p. 106—108°. (II) in cold Ac_2O with $HClO_4$ affords a carbonium *perchlorate*, m.p. 252—257°, whilst with warm Ac_2O, *mercurybis-(2-thiol-3-phenyl-2 : 3-dihydroquinazoline) diperchlorate*, m.p. 279—282°, is formed, identical with the perchlorate of (II). The Hg^{II} bromide of (II) similarly affords, in the cold, the *perchlorate*, m.p. 190—191°, of 2-thiol-4-hydroxy-3-phenyl-3 : 4-dihydroquinazoline mercuric dibromide, converted when warmed with Ac_2O into the *perchlorate*, m.p. 233°, of (III), which with $COMe_2$ affords (III). (IV) in the cold similarly yields a carbonium *perchlorate*, m.p. 207—208° (decomp.), which when heated gives the *monoperchlorate*, m.p. 219—221° (decomp.), of the bimol. form. The results are discussed in the light of recent work. J. L. D.

Action of phenols on quinoxalinic and acridinic anhydrides. P. Piutti [in part with G. B. Marini] (Gazzetta, 1936, **66**, 270—276).—Quinoxaline-2 : 3-dicarboxylic anhydride (I), when heated with PhOH or hydroxyphenols at 170°, gives Ph, m.p. 104°, and o-, m.p. 167°, m-, m.p. 175°, and p-*hydroxyphenyl quinoxaline-2-carboxylate*, m.p. 184°. At 110°, the reaction stops at the stage of *Ph*, m.p. 157°, and o-, m.p. 162°, m-, m.p. 202°, and p-*hydroxyphenyl quinoxaline-3-carboxylate-2-carboxylic acid*, m.p. 168°, all of which on further heating give the monocarboxylic esters. As a by-product, *quinoxaline-2-carboxylic acid*, m.p. 215° [also obtained by heating (I) alone], is formed. With N_2H_4,H_2O or $NHPh{\cdot}NH_2$, the monocarboxylic esters give *quinoxaline-2-carbohydrazide*, m.p. 204°, or *-phenylhydrazide*, m.p. 186°; PhOBz similarly gives $NHBz{\cdot}NH_2$. In none of these reactions was a phthalein obtained. Acridinic anhydride with phenols similarly gives no phthalein, but only decomp. products. E. W. W.

Action of selenium dioxide on β-diketones. P. Piutti (Gazzetta, 1936, **66**, 276—277).—$CH_2(COMe)_2$ and SeO_2 in EtOH give triketopentane, which with $o\text{-}C_6H_4(NH_2)_2$ yields *3-acetyl-2-methylquinoxaline*, m.p. 87—88°. $COMe{\cdot}CH_2{\cdot}COPh$ gives a product which is not Ph Me triketone. E. W. W.

Conversion of *ortho*- into *para*- and of *para*- into *ortho*-quinone derivatives. IV. Synthesis of furan derivatives of α- and β-naphthaquinones. S. C. Hooker and A. Steyermark (J. Amer. Chem. Soc., 1936, **58**, 1202—1207; cf. J.C.S., 1894, **65**, 717).—3-Hydroxy-2-αβ-dibromoethyl-, -2-αβ-dibromo-n-propyl-, m.p. 156—157° (decomp.), -2-αβ-*dibromo*-n-*butyl*-, m.p. 133—134°, and -2-αβ-*dibromo-β-phenylethyl*- (I), m.p. 172·5—173·5° (decomp.), -1 : 4-*naphthaquinones*, prepared from the 2-Δ^{α}-alkenyl derivatives and Br in $CHCl_3$, are converted by EtOH (usually boiling) into 5 : 6-benzcoumarone-3 : 4-quinone, m.p. 209·5—210° (*quinoxaline*, m.p. 195—196°), and its 1-*Me*, m.p. 164—164·5° (*quinoxaline*, m.p. 209·5—210·5°), 1-*Et*, m.p. 143·5—144° (*quinoxaline*, m.p. 159—160°), and 1-*Ph* (II), m.p. 219·5—220·5° (*quinoxaline*, m.p. 237—238°), derivatives, respectively. (I) is accompanied by a little *2-bromo-1-phenyl-5 : 6-benzcoumaran-3 : 4-quinone*, m.p. 218—219° (*quinoxaline*, m.p. 237—238°), whilst small amounts of (III) (below) and a *hydroxyphenylbenzcoumarone-3 : 4-quinone*, m.p. about 275° (decomp.), are formed with (II). 1-*Methyl*-, m.p. 246—247°, 1-*ethyl*-, m.p. 145—145·5°, and 1-*phenyl*- (III), 2 forms, both m.p. 246·5—247·5°, -4 : *5-benzcoumarone-3 : 6-quinone* are obtained when the isomeric 3 : 4-quinones (above) are treated with cold conc. H_2SO_4. Both series are cleaved by boiling 1% NaOH; 3-*hydroxy-2-acetonyl*-, m.p. 176·5—177·5° (IV), -2-*propionylmethyl*-, m.p. 165—165·5°, and -2-*phenacyl*-, m.p. 182·5—183·5°, -1 : 4-*naphthaquinone* are thus obtained. These are converted by conc. H_2SO_4 into the above 3 : 4- and then into the 3 : 6-quinones. (IV) is reduced (Adams) to 3-hydroxy-2-β-hydroxypropyl-1 : 4-naphthaquinone, m.p. 115·5—116·5° (cf. Fieser, A., 1927, 155). H. B.

Micro-hydrogenation by hyposulphite. E. Haas (Biochem. Z., 1936, **285**, 368—371).—A method is described, using methylene-blue, indigotindisulphonic acid, and Me-orange as test substances, which indicates the extent of reduction by $Na_2S_2O_4$ from pressure changes when the substance is mixed with a $NaHCO_3$–$Na_2S_2O_4$ solution in equilibrium with a CO_2–A atm. P. W. C.

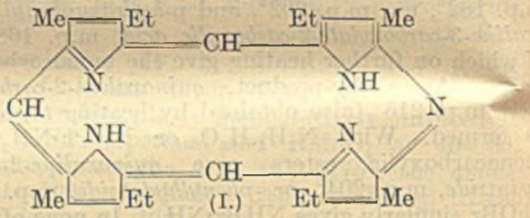
Synthesis of sulphur derivatives of 1 : 2 : 4-triazole. I. Matzurevitsch (Bull. Sci. Univ. Kiev, 1935, **1**, 9—83).—NH_2Ph and thiosemicarbazide (I) or $(NH_2{\cdot}CS{\cdot}NH{\cdot})_2$ (II) at 180° afford 3 : 5-dianilino-4-thiol-1 : 2-diazole and 3-amino-5-thiol-4-phenyl-1 : 2 : 4-triazole (III) (*dibenzyl* derivative, m.p. 189—190°). NH_2Ph and $(NHPh{\cdot}CS{\cdot}NH{\cdot})_2$ (at the b.p.) yield 3-anilino-5-thiol-4-phenyl-1 : 2 : 4-triazole (IV). NH_2Ph and $(o\text{-}C_6H_4Me{\cdot}NH{\cdot}CS{\cdot}NH{\cdot})_2$, m.p. 168—170° (decomp.) [from (I) and $o\text{-}C_6H_4Me{\cdot}NCS$], give (III) and (IV). *o*-Toluidine (V) and (I) or (II) afford *3-amino-5-thiol-4-*o*-tolyl-1 : 2 : 4-triazole*, $+H_2O$, m.p. 228—229° (*Ag* salt; *platinichloride*; 3-N-*Ac*, m.p. 190—191°, and 3-N-5-S-*dibenzyl* derivative, an oil), together with 3-amino-5-thiol-1 : 2-dihydro-1 : 2 : 4-triazole, its polymeride, not melting at 370°, and a no. of unidentified products; the corresponding 4-m-*tolyl*, $+H_2O$, m.p. 259—260° (*Ac* derivative, m.p. 188—189°), and 4-p-*tolyl* compound, $+H_2O$, m.p. 271—272° (*dibenzyl* derivative, m.p. 237—238°), are obtained similarly. (V) and $NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NHPh$ yield 3-o-*toluidino-5-thiol*-1 : 2 : 4-*triazole*, $+H_2O$, m.p. 219—222° (*Ac* derivative, m.p. 184—185°); the corresponding 3-m-, $+H_2O$, m.p. 247—248·5° (decomp.), 3-p-*toluidino*-, m.p. 263—264° (decomp.) (*Ac* derivative, m.p. 191—192°), and 3-*xylidino*-compound, $+H_2O$, m.p. 203—204°, were prepared analogously. $NH_2{\cdot}CH_2Ph$ and (I) (1·5 hr. at the b.p.) yield dibenzylthiocarbamide and an unidentified substance, m.p. 161—162°. The triazoles described give characteristic colorations with HNO_2 or with aq. $K_3Fe(CN)_6$. R. T.

Relations between reduction–oxidation potential and chemical constitution of flavins. R. Kuhn and P. Boulanger (Ber., 1936, **69**, [*B*], 1557—1566).—Lumiflavin is slightly more negative than lactoflavin (I) in the complete region, p_H 0·4—12·8. At p_H 7·0, (I) has E_0 0·185 volt. Investigation of 9-methyl-, 3 : 9-dimethyl-, 9-phenyl-, and 3-phenyl-

9-methylflavin and of 6 : 7-dimethyl- and 3 : 6 : 7-trimethyl-9-*d*-glucoflavin shows that methylation in position 3 has no appreciable influence. Me situated in the C_6H_6 nucleus has a marked effect. Displacement of Me from position 7 to 8 causes an increase of 0·113 volt in potential. Me groups at 6 and 7 occasion the most negative potentials observed among synthetic flavins. The influence of the pentitol chain is very slight. Replacement of 9-1′-ribityl by hydroxyethyl, dihydroxypropyl, *l*-1′-arabityl, *d*-1′-xylityl, or *d*-1′-sorbityl causes very slight positive increase in potential. An influence of the constitution and configuration of pentitol and hexitol chains could not be observed but differences are caused by the introduction of quite dissimilar groups, *e.g.*, Ph, $\cdot CH_2\cdot CO_2H$, $\cdot CH_2Ph$, and *cyclo*hexyl. Esterification of the vitamins with H_3PO_4 has as little effect on the redox potential as on the absorption spectrum. The yellow enzyme is 0·12 volt more positive than its pigment component. The sp. protein substance is therefore united not only to the phosphoric residue but also to the flavin nucleus. The probability that NH at 3 is concerned in the union is strengthened by the observations that the enzyme, in contrast with (I) and lactoflavinphosphoric acid, does not exhibit fluorescence and that 3-methyl-lactoflavin, in contrast with (I), does not promote the growth of rats on a vitamin-B_2-free diet. H. W.

Porphyrins. XXXVI. Vinyl- and amino-porphins. H. FISCHER, E. HAARER, and F. STADLER (Z. physiol. Chem., 1936, **241**, 201—219; cf. A., 1935, 362; this vol., 87).—The Me_2 ester of mesoporphyrin-IX in MeOH with NH_2OH at 135° for 12 hr. gives the *dihydrazide* (I), m.p. >300° (*Cu* salt; *compound* with 2PhCHO, m.p. 275°), which with HNO_2 at 0° yields the corresponding *diazide* (II). (II) with MeOH gives the corresponding *diurethane* (III), m.p. 252° (*Cu* salt, m.p. 270°), which with 10% HCl at 130—140° gives the *dihydrochloride*, m.p. >300°, of the corresponding diamine dihydrochloride [tetra-acetate (IV), m.p. 276°; *Cu* salt of (IV), m.p. 260°; *compound* (V) with Me_2SO_4, m.p. >300°]. (V) boiled for 3 hr. with 10% KOH in MeOH gives iso*protoætioporphyrin* (VI), m.p. >300° [*Cu* salt, m.p. >300°; *Fe* salt (VII), m.p. >300°]. (VII) with $Na+C_5H_{11}\cdot OH$ in H_2 gives the corresponding *chlorin*. (VI) reacts successively with $2CHN_2\cdot CO_2Et$ and CH_2N_2 to give a *substance*, m.p. 265°, with HI in AcOH to give *ætioporphyrin*-III, m.p. >300°, and with HBr in AcOH to give a *Br*-compound which yields hæmatoporphyrin on alkaline hydrolysis and a $(OMe)_2$-derivative, decomp. about 180°, with MeOH. The Fe salt of tetramethylhæmatoporphyrin with HI in AcOH and subsequent esterification with CH_2N_2 gives a *porphyrin*, m.p. 240° (*oxime*, m.p. 261°). (III) with 10% HCl gives the *hydrochloride* (VIII) of the corresponding amine. (VIII) after methylation with Me_2SO_4 yields (VI) on boiling with 10% KOH in MeOH. (I) in dil. H_2SO_4 oxidised with $KMnO_4$ and esterified with CH_2N_2 gives the ester (IX) of mesorhodin and (IX) on boiling with AcOH and esterifying with CH_2N_2 gives the *ester*, m.p. 252°, of mesoverdin. The Me ester of rhodoporphyrin-XV with NH_2OH gives the *monohydrazide* (X), m.p. 285°, and the Me_2 ester gives the *dihydrazide*, m.p. >360°, and (X). Similarly the Me_8 ester of uroporphyrin yields the *octahydrazide*, m.p. >360°, and the Me_8 ester of *iso*uroporphyrin-I yields the *octahydrazide*. The hydrazide of pyrroporphyrin-XV with PhCHO gives a *compound*, m.p. 290°. Phæophorbide and phæophytin heated with 30% KOH in MeOH at 180° for 6 hr. give a K salt which with Me_2SO_4 yields the Me ester of pyrroporphyrin. The Me_4 ester of coproporphyrin-I with NH_2OH gives the acid hydrazide, which with HNO_2 yields the acid azide (XI). (XI) boiled with 50% AcOH gives the *hexahydrochloride* (XII) of the corresponding *amine* [*octa-acetate* (XIII), m.p. 287°; *Cu* salt of (XIII), m.p. 278°]. (XII) with Me_2SO_4 and KOH in MeOH gives 1 : 3 : 5 : 7-*tetramethyl*-2 : 4 : 6 : 8-*tetravinylporphyrin* (XIV), m.p. >360° (*Cu* salt, m.p. >360°), with elimination of NMe_3. (XIV) in AcOH with $Pd+H_2$ gives ætioporphyrin-I. W. McC.

Imidoporphyrins. II. Synthesis of monoimidoætio- and monoimidocopro-porphyrin. H. FISCHER and W. FRIEDRICH (Annalen, 1936, **523**, 154—164).—5 : 5′-Dibromo-4 : 4′-dimethyl-3 : 3′-diethylpyrromethene hydrobromide is converted by NaOH in H_2O–C_5H_5N at 130—140° into *monoimidoætioporphyrin* (I), m.p. >300° (*Cu* salt), and a



(I.)

(?) *di-imidoætioporphyrin*. Similarly 5 : 5′-dibromo-4 : 4′-dimethylpyrromethene-3 : 3′-dipropionic acid hydrobromide affords monoimidocoproporphyrin, transformed by CH_2N_2 into the *Me_4* ester, which sinters from 240°. Under like conditions 5-bromo-4 : 3′ : 5′-trimethyl-3-ethylpyrromethene-4′-propionic acid hydrobromide passes into mesoporphyrin and *monoimidomesoporphyrin*, and 5 : 5′-dibromo-3 : 3′ : 4 : 4′-tetramethylpyrromethene hydrobromide into *monoimido-octamethylporphin*. H. W.

Chlorophyll. LXVIII. Ketophylloporphyrins and their transition into deoxophyllerythrin derivatives. H. FISCHER, K. MÜLLER, and O. LESCHHORN (Annalen, 1936, **523**, 164—198).—The Fe salt of phylloporphyrin Me ester (I) is converted by $SnBr_4$ in $(C_2H_4Cl)_2O$ into formylphylloporphyrin Me ester (II), m.p. 236° (*Fe*, m.p. 245°, and *Cu*, m.p. 208°, salts), the *oxime*, m.p. 257°, of which is transformed by boiling Ac_2O containing KOAc into 6-*cyanophylloporphyrin Me ester*, m.p. 255° (*Cu* salt, m.p. 256—257°), which could not be hydrolysed satisfactorily. (II) and anhyd. HCN in C_5H_5N containing K_2CO_3 give 6-*formylphylloporphyrin-cyanohydrin Me ester*, m.p. 236°. Condensation of (II) with $CH_2(CO_2H)_2$ in C_5H_5N containing piperidine under mild conditions gives the tricarboxylic acid (*Me_3* ester, m.p. 255°), whereas under more drastic circumstances deoxophyllerythrin-9-acetic acid (*Me* ester, m.p. 233°) is obtained. (II) and MeOH–conc. HCl at 60° afford 9-*methoxydeoxophyllerythrin Me ester* (III), m.p. 222—223°. Boiling C_5H_5N containing Na_2CO_3 converts (II) into 9-*hydroxydeoxophyllerythrin Me ester* (IV), m.p. 276° (*Cu* salt, m.p. 228°; *Bz* derivative, m.p. 253°; *acetate*, m.p. 234°). Treatment of (IV) with boiling $CHCl_3$–MeOH containing I affords 9 : 10-*dimethoxydeoxophyllerythrin ester*, m.p. 220°, and 10-*methoxyphyllerythrin ester*, m.p. 268° (*oxime*). (III) and $CH_2Ph\cdot OH$ containing I at 100° yield *benzyloxydeoxophyllerythrin ester*, m.p. 228°. HI (*d* 1·96) in AcOH at 65—70° converts (III) or (IV) into *deoxophyllerythrin*, m.p. 276—277°. (I), Bz_2O, and $SnBr_4$ at 70° yield 6-*benzoylphylloporphyrin Me ester* (V), m.p. 303° (*Cu*, m.p. 258°, and *Fe*, m.p. 262°, salts). 9-*Hydroxy-9-phenyldeoxophyllerythrin Me ester*, m.p. 278°, from (V) and boiling KOH–MeOH, is converted by HI (*d* 1·96) in AcOH at room temp. into 9-*phenyldeoxophyllerythrin Me ester*, m.p. 258°. (II) and $CH_2(CN)_2$ in C_5H_5N containing piperidine at 100° afford 9-*dicyanomethyldeoxophyllerythrin Me ester*, m.p. 222°. The Fe salt of (II) is reduced by Na and boiling *iso*-$C_5H_{11}\cdot OH$ to deoxophyllerythrin.

[With O. Leschhorn.] Chloroporphyrin l_4 Me_2 ester is converted by NaOEt in boiling C_5H_5N–xylene and treatment of the product with CH_2N_2 into phylloerythrin. 3-Carbethoxy-5-formyl-4-methylpyrrole-2-propionic acid and hæmopyrrole in AcOH at 0° yield 4-*carbethoxy*-4′ : 5′ : 3-*trimethyl*-3′-*ethylpyrromethene-5-propionic acid* (VI), m.p. 61° [*Me* ester (VII), m.p. 165° (decomp.); *hydrobromide*, m.p. 204° (decomp.)]. Bromination of (VI) and (VII) gives products, m.p. 202° (decomp.) and m.p. 112°, respectively, but the action is accompanied by partial decarboxylation. Hæmopyrrolealdehyde, 3-carbethoxy-4-methylpyrrole-2-propionic acid, and HBr afford 4 : 5 : 4′ : 5′-*tetramethyl*-3 : 3′-*diethylpyrromethene hydrobromide*, m.p. 218°. H. W.

Derivatives of blood-pigments. A. Hamsik (Z. physiol. Chem., 1936, **241**, 156—167; cf. A., 1930, 1304; 1931, 745; Langenbeck, A., 1932, **412**, 757).—Amorphous and cryst. hæmatin (I) with cold 80% HCO_2H gives formyl- and with AcOH acetyl-hæmin whilst the anhydride (II) and the half anhydride (III) do not react. Probably (II) and (III) are produced by loss of the OH attached to Fe. (I), (II), and (III) differ in solubility in C_5H_5N and 5% aq. $NaHCO_3$. The properties of (I) and the prep. of (III), glyoxaline-, histidine-, and pyridine-hæmatin, and the following derivatives of hæmin: glyoxaline-chloro- and -formyl-, pyridine-, pyridine-formyl-, -acetyl-, and -chloro-, and the K salt of protoporphyrin are described. W. McC.

Fluorescence of the chlorophyll series. Reversible reduction of chlorophyll-*a* and -*b*. V. M. Albers, H. V. Knorr, and P. Rothemund (Physical Rev., 1935, [ii], **47**, 198; cf. A., 1935, 12).—Chlorophyll-*a* and -*b* were reduced in C_5H_5N under an atm. of N_2 or CO_2, and reoxidised in air. The reduced chlorophyll (I) showed no characteristic absorption in the visible region. The absorption spectra of the original and reoxidised (I) were identical in the visible region. The fluorescence spectra of the reduced, re-oxidised, and original (I) were all different, and fluorescence was more intense in the original (I). The fluorescence spectra for the reduced and reoxidised (I)-*a* and -*b* are different according as CO_2 or N_2 is used. L. S. T.

Spectroscopic studies of simpler porphyrins.—See this vol., 1048.

Fluorescence of the porphyrins.—See this vol., 1048.

Compounds of pyrrole with furfuraldehyde. I. Furfurylidenepyrroles. P. Piutti (Gazzetta, 1936, **66**, 265—270).—2 : 4-Dimethyl-3-ethylpyrrole (I) with furfuraldehyde, AcOH, and a trace of HBr gives the 5-*furfurylidene* derivative (II), m.p. 185°, of (I). With a larger proportion of HBr, the *hydrobromide*, m.p. 83—84°, of (II) is formed, and is converted into the *picrate*, decomp. 154°, and the *perchlorate*, m.p. 217° (decomp.). 3-*Acetyl-5-furfurylidene-2 : 4-dimethylpyrrole perchlorate*, 2-*furfurylidenetetrahydroskatole picrate* [both of which decompose without melting (up to 280°)], and 5-*furfurylidene-2 : 4-dimethylpyrrole hydrobromide*, m.p. $\nless$ 280°, are prepared similarly. E. W. W.

***iso*Oxazole group. Action of nitric acid on unsaturated compounds. XIII—XV. Products of the reacton of nitric acid with citraconic acid.** A. Quilico and R. Fusco (Gazzetta, 1936, **66**, 278—286, 287—293, 293—299).—XIII. Eulite (I) (cf. this vol., 617), of which the prep. is modified, when dissolved in MeOH–NaOMe and treated with $HgCl_2$ gives a *mercurichloride*, $C_6H_6O_8N_4Cl_2Hg_2$. The base *A*, $C_6H_9O_2N_3$, m.p. 136—137°, obtained by $SnCl_2$ reduction of (I) (*loc. cit.*) is identified as 3-*methyl*-5-(β-*amino*-α-*oximinoethyl*)isoo*xazole* (II) (*Ac* derivative, m.p. 152°), which on prolonged boiling with HCl yields NH_2OH and 5-*glycyl*-3-*methyl*iso*oxazole hydrochloride* (III) [p-*nitrophenylhydrazone*, m.p. 215—216° (decomp.)]. The last is converted by NaOH into a yellow *base*, 2 : 5-(3′ : 3″-*dimethyl*-5′ : 5″-*di*iso*oxazolyl*)*dihydropyrazine* (IV), m.p. 173—174° (*Ac* derivative, m.p. 220°). The second base, *B*, $C_6H_{11}ON_3$ (*loc. cit.*), from (I) is identified as 3-*methyl*-5-(αβ-*diaminoethyl*)iso*oxazole* (Ac_2 derivative, m.p. 184°). A third *base*, *C*, $C_6H_9O_2N_3$, m.p. 165—166° (*Ac* derivative, m.p. 239°), is also isolated, and with HNO_2 gives a *diazo-acid*, $C_6H_5O_3N_3$. It is concluded that (I) is 3-*methyl*-5-(ααβ-*trinitroethyl*)iso*oxazole*.

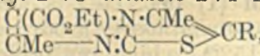
XIV, XV. Thermal decomp. of (I) mixed with powdered glass gives, with N_2O_3, HCN, AcOH, MeCN, and $MeNO_2$, 5-*nitroacetyl*-3-*methyl*iso*oxazole* (V), m.p. 37°, b.p. 132—133°/25 mm. [*phenylhydrazone*, m.p. 111° (decomp.); p-*nitrophenylhydrazone*, m.p. 165° (decomp.); *semicarbazone*, m.p. 197—198° (decomp.)]. The *oxime*, m.p. 98° [*Bz* derivative, m.p. 185—190° (decomp.)], of (V) is reduced ($SnCl_2$) to (II) (above); (V) is similarly reduced to (III). (V) condenses with aldehydes in presence of NH_2Me, thus giving 5-α-*nitro-cinnamoyl*-, m.p. 120° [p-*nitrophenylhydrazone*, m.p. 225° (decomp.)], and -p-*methoxycinnamoyl*-3-*methyl*iso*oxazole*, m.p. 130° (decomp.) [p-*nitrophenylhydrazone*, m.p. 227° (decomp.)]. Diphenyldihydropyrazine forms an *Ac* derivative, m.p. 190°. E. W. W.

Preparation of morpholine. L. Médard (Bull. Soc. chim., 1936, [v], **3**, 1338—1343; cf. A., 1897, i, 314; 1898, i, 601).—$NH(CH_2\cdot CH_2\cdot OH)_2$ with 0·55 part of conc. H_2SO_4 at 175—180° affords morpholine, isolated as the hydrochloride, in nearly theoretical yield. The free base is difficult to obtain anhyd. J. L. D.

Amides and urethanes derived from morpholine. L. Médard (Bull. Soc. chim., 1936, [v], **3**, 1343—1347).—HCO_2H with aq. morpholine (I) affords N-*formylmorpholine*, b.p. 234°/760 mm. The following are also prepared: N-*acetyl*-, b.p. 242·2—242·6°/759 mm., N-*propionyl*-, b.p. 249°/760 mm., N-*butyryl*-, m.p. 27°, and N-*hexoyl-morpholine*, b.p. 293°/760 mm. (I) with $ClCO_2Me$ in aq. Na_2CO_3 affords *morpholine methylcarbamate*, b.p. 212·3—212·8°/759 mm. Et (A., 1898, i, 601), *Pr*, b.p. 238°/760 mm., and *morpholine butylcarbamate*, b.p. 252—252·5°/760 mm., are also prepared. J. L. D.

N-Hydroxyaryl-substituted morpholines.—See B., 1936, 716.

3 : 4 : 5 : 6-Tetrahalogeno-2-amino-1-hydroxybenzenes.—See B., 1936, 685.

Synthesis of thiazologlyoxaline and thiazolopurine derivatives. E. Ochiai (Ber., 1936, **69**, [*B*], 1650—1655).—Treatment of Et 2-thiol-4-methylglyoxaline-5-carboxylate with CH_2ClAc in EtOH in presence or absence of NaOEt affords *Et 2-acetonylthiol-4-methylglyoxaline-5-carboxylate*, m.p. 108—109° (*hydrochloride*, decomp. 171°; *semicarbazone*, decomp. 140°), which is converted by boiling $POCl_3$ into *Et 4′-methyl-2′ : 3′-thiazolo-2 : 1-4-methylglyoxaline-5-carboxylate*,  $\begin{matrix}C(CO_2Et)\cdot N\cdot CMe \\ CMe\text{——}N{:}C\text{——}S\end{matrix}\!>\!CR$, m.p. 146—147°, and by boiling Ac_2O containing anhyd. NaOAc into *Et 5′-acetyl-4′-methyl-2′ : 3′-thiazolo-2 : 1-4-methylglyoxaline-5-carboxylate*, m.p. 205° (p-*nitrophenylhydrazone*; *oxime*, decomp. 256°). 8-Chlorotheophylline and NaHS in H_2O at 150—155° give 8-*thioltheophylline*, decomp. 320—321°, transformed by NaOEt and CH_2ClAc into 8-*acetonylthioltheophylline* (I), m.p. 204—205° (*oxime*, decomp. 244° after blackening at about 230°), which is converted by $POCl_3$ into 4′-*methyl*-2′ : 3′-*thiazolo*-8 : 7-*theophylline*, m.p. 263°. The attachment of $\cdot CH_2Ac$ to S in (I) is established by the observation that 8-thioltheophylline is converted by EtBr in boiling EtOH into 8-*ethylthioltheophylline*, m.p. 249°, which is not desulphurised by $NaNO_2$ and requires treatment with 20% NaOH to cause loss of EtSH. *Et 2-ethylthiol-4-methylglyoxaline-5-carboxylate*, m.p. 144—145°, is described. H. W.

Anthraquinone derivatives. Anthrathiazole-anthraquinonecarboxylimides.—See B., 1936, 686.

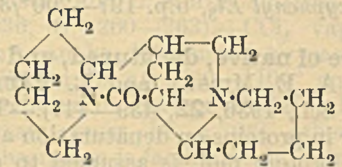
Structure of vitamin-B_1.—See this vol., 1159.

Structure of cyanine dyes, and their optical and photographic properties II. Thiocyanines with sulphur-containing substituents. A. I. Kiprianov, Z. P. Sitnikov, and E. D. Sitsch (J. Gen. Chem. Russ., 1936, **6**, 576—583).—*p*-Methylthiolacetanilide and P_2S_5 at 115° yield p-*methylthiolthioacetanilide*, m.p. 114—115°, from which the expected benzthiazole derivative was not obtained by oxidation with $K_3Fe(CN)_6$. 1-Methylbenzthiazole and HNO_3–H_2SO_4 afford 5-*nitro*-1-*methylbenzthiazole*, m.p. 164—165°, reduced by $SnCl_2$ in HCl to the 5-*NH_2*-compound, m.p. 122°, which is diazotised and treated at 70° with aq. K_2CS_3, the xanthate obtained is boiled with EtOH–KOH, and the product is treated with Me_2SO_4, to yield 5-*methylthiol*-1-*methylbenzthiazole*, the *ethiodide*, m.p. 215°, of which yields 5 : 5′-*dimethylthiol*-2 : 2′-*diethylthiocarbocyanine iodide* (I) with Et orthoformate and C_5H_5N (1·5 hr. at the b.p.), and the 8-*Me* derivative of (I) when treated with Et orthoacetate and C_5H_5N (1·5 hr. at the b.p.). NaSMe in EtOH yields *methylthiolpyruvonitrile*, $SMe\cdot CH_2\cdot CO\cdot CN$ (II), b.p. 74·5°/20 mm., with $CH_2Cl\cdot CO\cdot CN$, and *Et ethylthiolpyruvate*, b.p. 174—176°, with $CH_2Cl\cdot CO_2Et$. (II) and EtOH–HCl yield β-*methylthiolethyliminoether hydrochloride*, $SMe\cdot CH_2\cdot C(OEt){:}NH,HCl$, readily decomp. in EtOH to afford *Et methylthiolorthoacetate*, $SMe\cdot CH_2\cdot C(OEt)_3$, b.p. 78—80°/30 mm., which condenses with 1-methylbenzthiazole ethiodide (III) in C_5H_5N or EtOH to yield 2 : 2′-*diethyl*-8-*methylthiolmethylcarbothiocyanine iodide*. The corresponding 8-*SEt* derivative is prepared from (III) and β-*ethylthiolethyliminoether*, $SEt\cdot CH_2\cdot C(OEt){:}NH$, b.p. 103—104° (prepared as above from *ethylthiolpyruvonitrile*, b.p. 104—105°). Introduction of S-containing groups into carbothiocyanine dyes does not affect their sensitising and stabilising properties. R. T.

Alkaloids of *Heliotropium lasiocarpum*. VI. Synthesis of pyrrolidine derivatives. G. Menschikov and J. Schdanovitsch (Ber., 1936, **69**, [*B*], 1799—1802).—Addition of $Pr^{\beta}CN$ to a solution of Mg and $OMe\cdot[CH_2]_3\cdot I$ in Et_2O gives η-*methoxy*-β-*methylheptan*-δ-*one*, b.p. 198—199°/1 atm., the *oxime*, b.p. 124—125°/12 mm., of which is reduced by Na and $Bu^{\beta}OH$ to δ-*amino*-η-*methoxy*-β-*methylheptane* (I), b.p. 200·5—201°/1 atm. (I) is converted by 50% HBr at 150—155° into 2-iso*butylpyrrolidine*, b.p. 163—164°/1 atm., which with CH_2O and HCO_2H affords 1-*methyl*-2-iso*butylpyrrolidine* (I), b.p. 163·5—165°/1 atm. (*picrate*, m.p. 138—139°; *platinichloride*, m.p. 138—140°). 1-Methyl-2-*n*-butylpyrrolidine (II) is obtained similarly from $Pr^{a}CN$. Neither (I) nor (II) is identical with *dl*-dihydrode-*N*-methylheliotridane. H. W.

Lupin alkaloids. X. Synthesis of *dl*-oxysparteine. G. R. Clemo, W. McG. Morgan, and R. Raper (J.C.S., 1936, 1025—1028; cf. A., 1933, 841).—Attempted Claisen condensation of 2 mols. of Me pyridyl-2-acetate under varying conditions yields *complexes*, m.p. 177° and 295°, only. Et piperidyl-2-acetate (I), $ClCO_2Et$, and Na_2CO_3 (18 hr.; room temp.) afford *Et 1-carbethoxypiperidyl-2-acetate*, b.p. 148—150°/9 mm., converted into the *acid*, m.p. 65°, by refluxing with C_6H_6–NaOEt (6 hr.) followed by conc. HCl (12 hr.; 100°). (I) with $CH(OEt)_3$ and Ac_2O (2 hr.; reflux) yields 1-*carbethoxy*-4-*keto*-3-(2′-*pyridyl*)*pyridocoline*, b.p. 250—255°/1 mm., m.p. 126° (*picrate*, m.p. 216°), reduced (Pt–AcOH–H_2 at 100 lb. per sq. in.) to impure 1-*carbethoxy*-4-*keto*-3-(2′-*piperidyl*)*octahydropyridocoline*, b.p. 200—210°/1 mm.; this on Bouveault reduction forms the corresponding 1-*carbinol*, which with PBr_5 gives

1-*bromomethyl-4-keto-3-(2′-piperidyl)octahydropyridocoline*, converted by heating with K_2CO_3 (18 hr.; 100°) into *dl*-oxysparteine (II) [methiodide, m.p. 203—204°; *hydriodide*, m.p. 275° (decomp. 345°)], identical with that obtained by oxidation [NaOH–$K_3Fe(CN)_6$] of *dl*-sparteine (A., 1928, 1030). The structure of (II) is hence as shown.



(II.)

F. N. W.

Lupin. XI. Alkaloids of *Lupinus barbiger*, S. Wats. J. F. Couch (J. Amer. Chem. Soc., 1936, **58**, 1296—1299).—Sparteine [*dihydrobromide* (+H_2O), m.p. 197°; *methiodide*, m.p. 239—240°; *zincichloride*, m.p. 316—317°], *dilupine* (I), provisionally $C_{16}H_{26}O_2N_2$, an oil, $[\alpha]_D^{26}$ +65·59° in H_2O (*hydrobromide*, m.p. 233—234°), *trilupine* (II), $C_{15}H_{24}O_3N_2,2H_2O$, m.p. (anhyd.) 252°, $[\alpha]_D^{30}$ +63·76° in H_2O [*platinichloride* (+$4H_2O$), m.p. 224° (decomp.); *aurichloride* (+$4H_2O$), m.p. 188—189° (decomp.)], and basic and much resinous material are isolated (method: A., 1935, 97) from the dry plant. (I) and MeI give a *methiodide*, $C_{16}H_{26}ON_2$,MeI, m.p. 253°, suggesting that (I) is a *C*-methyl-lupanine *N*-oxide. (II) is probably *d*-lupanine 1 : 9-dioxide (for nomenclature, see this vol., 741). Thus, (II) heated with acids affords the salts of *d*-lupanine (III) [*dihydrochloride* (+H_2O), m.p. 163—164°; *aurichloride*, m.p. 206°], whilst (III) is oxidised (CaO_2,H_2O) to (II). (II) and MeI give (probably) the 9-*methiodide*, m.p. 127°, of *d*-lupanine 1-oxide.

H. B.

Cocaine syntheses from hyoscyamine. I. Preparation of tropinonecarboxylic esters. N. A. Preobrashenski, M. N. Schtschukina, and R. A. Lapina (Ber., 1936, **69**, [*B*], 1615—1618).—Tropinone and Et_2CO_3 condense readily in the presence of molten Na to Et tropinonecarboxylate (+$2H_2O$), m.p. 64—65° (corresponding *picrate*, m.p. 151°). With Me_2CO_3 the production of Me tropinonecarboxylate (+$2·5H_2O$), m.p. 96—98° (corresponding *picrate*, m.p. 163—164°), is better achieved with the more readily fusible K. Both condensations are preferably performed in an inert solvent of suitable, high b.p., *e.g.*, xylene.

H. W.

Amine oxides of alkaloids. X. Action of hydrogen peroxide on hydrastinine and hydrohydrastinine. XI. *NN′*-Dioxide of *NN′*-dimethylpiperazine. XII. *N*-Oxide of sparteine. Max and Michel Polonovski (Bull. Soc. chim., 1936, [v], **3**, 885—888, 888—891, 891—898).—X. Hydrastinine (I) with $COMe_2$–H_2O_2 gives dehydrohydrastinine and hydrastinine anhydride, whilst hydrohydrastinine (II) yields its N-*oxide* (*hydrochloride*, m.p. 199—200°; *hydrobromide*, m.p. 174—175°), converted by SO_2 into a *N*-sulphonic ester, (I), and (II). The formation of (I) is interpreted by means of a mol. transposition.

XI. Dimethylpiperazine with H_2O_2–$COMe_2$ gives its NN-*dioxide*, m.p. 269° from $CHCl_3$ and m.p. 239° from EtOH (*dihydrochloride*, m.p. 208—209°), from which the base is regenerated by SO_2 and by Zn–HCl. It is acid to litmus and slightly alkaline to Me-orange, and may be determined by silicotungstic acid.

XII. Dioxysparteine (III) (A., 1887, 1056; 1897, 231), obtained from sparteine and H_2O_2–$COMe_2$ and previously considered to be an *NN*-dioxide (cf. A., 1919, i, 414), is shown to be *sparteine* N-*monoxide hydrate*, m.p. 129° [*hydrobromide*, m.p. 138°; *hydriodide* (IV), m.p. 147°; *dihydrochloride*, m.p. 153°; *dihydrobromide*, m.p. 155°; *dinitrate*, m.p. 97—98°; *dipicrate*, m.p. 150°], which with KI gives (IV). The alleged methiodide of (III) (cf. *loc. cit.*) is shown to be (IV). The above di-salts lose some acid at 100° [cf. the alleged product, $C_{15}H_{26}O_2N_2$,1·5HBr,H_2O (*loc. cit.*)].

H. G. M.

Alkaloids of Chinese *Corydalis* tubers. (*Corydalis ambigua*, "Yen-Hu-So"). M. Huang (Ber., 1936, **69**, [*B*], 1737—1745).—The drug is moistened with $Al_2(SO_4)_3$ solution and extracted with C_6H_6, thus yielding corydaline, m.p. 134—135°, and unidentified bases and considerable amounts of a volatile oil containing small amounts of crystals, m.p. 84—86°, which are not identical with cedrol and are possibly dimyristyl alcohol. Renewed extraction of the residue with C_6H_6 after saturation of it with NH_3 gives protopine, corybulbine, *r*-tetrahydropalmatine (identical with the corydalis *B* of Chou), *r*-tetrahydrocoptisine (corydalis *E*), and *l*-tetrahydrocoptisine (corydalis *D*). Extraction of the residue with EtOH yields coptisine and mesocorydaline.

H. W.

New alkaloids of ergot: ergosine and ergosinine. S. Smith and G. M. Timmis (Nature, 1936, **137**, 1075).—By treatment with acids $C_{30}H_{35}O_5N_5$ (this vol., 351) ("ergosinine") is converted into an isomeride, *ergosine*, decomp. 228°, $[\alpha]_{5461}^{20}$ −194° in $CHCl_3$.

L. S. T.

Alkaloids of *Fritillaria roylei*. I. Isolation of peimine. Y. F. Chi, Y. S. Kao, and K. J. Chang (J. Amer. Chem. Soc., 1936, **58**, 1306—1307).—Details are given for the isolation of peimine (I), $C_{26}H_{43}O_3N$ (not $C_{19}H_{30}O_2N$; cf. Chou and Chen, A., 1932, 1178), m.p. 224° [*hydrochloride*, m.p. 295° (decomp.); *hydrobromide*, m.p. 293·5—294°; *H sulphate*, m.p. 278—280°; *platinichloride*, m.p. 233—235° (decomp.); *aurichloride*, m.p. 164—165°], from the corms. Verticin (*loc. cit.*) is probably (I).

H. B.

New derivatives of *p*-arsanilic acid. VII. *p*-Arsonoazelanilic and *p*-arsonosebacanilic acids and related compounds. G. T. Morgan and E. Walton (J.C.S., 1936, 902—905; cf. A., 1935, 768).—With $SOCl_2$ Me H azelate yields its acid *chloride*, b.p. 150—155°/15 mm., which with Na *p*-arsanilate yields *Me* p-*arsonoazelanilate* (I) (*Na* salt). The *Et* compound (II) was similarly obtained through the acid *chloride*; b.p. 156—160°/20 mm. (I) and (II) are hydrolysed to the corresponding *acid*, which with SO_2–HCl affords crude p-*dichloroarsinoazelanilic acid*, hydrolysed to p-*oxyarsinoazelanilic acid*. The following *amides*, *p*-$AsO_3H_2·C_6H_4·NH·CO·[CH_2]_7·COR$, were prepared from (I) and the corresponding amine: R=NH_2 [*Na* salt (+H_2O)], NHMe (*Na* salt), NHEt [*Na* salt (+$3H_2O$)]. Azelayl dichloride and Na *p*-arsanilate afford *azelanilide*-pp′-*diarsonic acid* (Na_2

salt). With $SOCl_2$ Me H sebacate (modified prep.) yields its acid *chloride* (III), b.p. 177°/23 mm., which with Na *p*-arsanilate forms *Me* p-*arsonosebacanilate* (*Na* salt). The *Et* compound (*Na* salt) was similarly prepared. These esters are hydrolysed to the *acid* [*Na* salt ($+H_2O$)], which affords p-*dichloroarsinosebacanilic acid*, m.p. 130—135°, hydrolysed to p-*oxyarsinosebacanilic acid*. The following *amides*, $AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}[CH_2]_8{\cdot}COR$, are described: $R=NH_2$ [*Na* salt ($+H_2O$)], NHMe [*Na* salt ($+H_2O$)], NMe_2 (*Na* salt). (III) with NH_2Ph gives *Me sebacanilate*, m.p. 67—68° (free *acid*, m.p. 121—122°). The corresponding acid *chloride* with *p*-arsanilic acid (at 150°) forms *sebacanilide*-p-*arsonic acid* (*Na* salt). Sebacyl dichloride with Na-*p*-arsanilate and Na_2CO_3 affords *sebacanilide*-pp′-*diarsonic acid* (*Na_2* salt). The Na salts of these compounds have a higher toxicity than those of the earlier series (A., 1931, 636; 1933, 290) but there is no increase in curative action.

F. N. W.

Organic compounds of mercury. XIII. Preparation of a new type of asymmetric organic mercury compounds as proof of the structure of alkanol- and β-alkyloxyalkyl-mercuri-salts. A. N. Nesmejanov and R. C. Friedlina (Ber., 1936, **69**, [*B*], 1631—1635).—Confirmation of Hofmann's formulation of alkanol- and β-alkyloxyalkyl-mercuri-salts is found in their reaction with Sn aryl halides thus: $2OH{\cdot}CH_2{\cdot}CH_2{\cdot}HgX+SnAr_2X_2+4NaOH=2OH{\cdot}CH_2{\cdot}CH_2{\cdot}HgAr+H_2SnO_3+4NaX+H_2O$. Thus Sn *p*-ditolyl dichloride and $OH{\cdot}CH_2{\cdot}CH_2{\cdot}HgBr$ in boiling EtOH containing KOH afford *Hg* p-*tolyl* β-*hydroxyethyl*, m.p. 52·5—53·5°, quantitatively converted by 15% HCl into C_2H_4 and *p*-$C_6H_4Me{\cdot}HgCl$. *cyclo*Hexene (I) and $Hg(OAc)_2$ in H_2O give o-*hydroxyacetomercuri*cyclo*hexane*, m.p. 112·5—113°, transformed by $SnPh_2Cl_2$ into *Hg Ph* o-*hydroxy*cyclo*hexyl*, m.p. 101—102°. (I) and $Hg(OAc)_2$ in EtOH yield o-*ethoxyacetomercuri*cyclo*hexane*, m.p. 79° after softening at 76°, whence *Hg Ph* o-*ethoxy*cyclo*hexyl*. Chloromercurimethyldihydrobenzofuran and $SnPh_2Cl_2$ yield 1-*phenylmercurimethyl*-1 : 2-*dihydrobenzofuran*, m.p. 60—61°. PhNCO and $OH{\cdot}CH_2{\cdot}CH_2{\cdot}HgBr$ in boiling C_6H_6 afford *bromomercuriethyl phenylcarbamate*, m.p. 124—126°.

H. W.

Mercury derivatives of azo-dyes. W. Braker and W. G. Christiansen (J. Amer. Pharm. Assoc., 1936, **25**, 499—501).—*p*-Aminophenylmercuriacetate, diazotised and coupled with *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$ in dil. NaOH affords 4-*hydroxymercuri*-2′-*amino*-4′-*hydroxyazobenzene*; similarly *o*-$NO_2{\cdot}C_6H_4{\cdot}OH$ yields 4-*hydroxymercuri*-3′-*nitro*-4′-*hydroxyazobenzene*. These substances are too insol. for therapeutic use.

F. O. H.

Reactions of hexaethyldistannane and diethylstannane with organic mercury compounds as a method of preparing organic compounds of tin with substituents in the benzene nucleus. K. A. Kozeschkov, A. N. Nesmejanov, and V. P. Pusireva (Ber., 1936, **69**, [*B*], 1639—1642).—Reactions are described which proceed according to the schemes: $Sn_2R_6+HgAr_2=2SnR_3Ar+Hg$; $Sn_2R_6+HgArCl=SnR_3Ar+Hg+SnR_3Cl$ (where $Ar=Ph$, $OH{\cdot}C_6H_4{\cdot}$, or $NMe_2{\cdot}C_6H_4{\cdot}$ and $R=Et$) and $Sn_2R_6+HgCl_2=2SnR_3Cl+Hg$ or $SnR_2+HgCl_2=SnR_2Cl_2+Hg$. The compounds, SnR_3Ar, are heavy, colourless liquids which first lose Ar under the action of Br or $Hg^{\cdot\cdot}$ solutions. They reduce $AgNO_3$–EtOH or $PtCl_4$. The following are new: *Sn* p-*dimethylaminophenyl Et*$_3$, b.p. 172—173°/3 mm. (complex *compound* with $AuCl_3$); *substance* $SnEt_3Br,2NH_3$; *Sn* p-*hydroxyphenyl Et*$_3$, b.p. 197—200°/3 mm.

H. W.

Structure of native, denatured, and coagulated proteins. A. E. Mirsky and L. Pauling (Proc. Nat. Acad. Sci., 1936, **22**, 439—447).—The changes which occur in proteins on denaturation are reviewed. The native protein mol. is assumed to consist of a polypeptide chain, folded into a uniquely defined configuration in which it is held by H-linkings between the peptide N and O atoms, and between the free NH_2 and CO_2H of the diamino- and dicarboxyl amino-acid residues. The denatured protein mol. is characterised by the absence of a uniquely defined configuration, and thus lacks sp. properties. This view is supported by the difference of entropy between native and denatured proteins, and the heat change and activation energy of denaturation. Reagents causing denaturation [*e.g.*, EtOH, $CO(NH_2)_2$] are substances which affect H-linking formation. The action of ultra-violet light on the native protein mol. is to cause a break in the mol. so that it can be denatured at a lower temp. after illumination than before. Dehydration consists primarily in the coagulation of the protein mols. without loss of their special configurations.

A. J. M.

Glucoproteins. II. Polysaccharides of vitreous humour and of umbilical cord.—See this vol., 1138.

Apparatus for the microhydrogenation of organic compounds. H. Jackson and R. N. Jones (J.C.S., 1936, 895—899).—An improvement of the apparatus of Smith (A., 1932, 619), the method of shaking being modified, the means of introducing the substance improved, and complete compensation for temp. changes made.

F. R. S.

Application of Andrews' iodine monochloride method to the iodine bromide process.—See this vol., 1081.

Recent advances in micro-analysis. II. Functional analysis. (Mlle.) A. Lacourt (Bull. Soc. chim. Belg., 1936, **45**, 313—333; cf. this vol., 1080).—A review of methods for determining various org. groups.

R. C. M.

Determination of hydroxyl groups in organic compounds. M. Freed and A. M. Wynne (Ind. Eng. Chem. [Anal.], 1936, **8**, 278—279).—The substance is heated to the b.p. with 2 c.c. of 20% C_5H_5N–Ac_2O reagent, cooled, boiled with H_2O for 5 min., and the AcOH titrated with NaOH (cresolphthalein), if necessary after adding EtOH to facilitate dissolution. Accurate results are obtained with most substances except sugar alcohols (2·5% low) and *tert.*-alcohols (no reaction).

S. C.

Micro-determination of acetyl groups. A. Elek and R. A. Harte (Ind. Eng. Chem. [Anal.], 1936, **8**, 267—269).—4—10 mg. of substance are hydrolysed with *p*-$C_6H_4Me{\cdot}SO_3H$, the resultant solution is evaporated to dryness in vac., and AcOH and SO_2 determined in the distillate iodometrically. A suitable apparatus is described. The method is relatively simple and accurate. S. C.

Determination of the concentration of vaporised carbon tetrachloride. J. C. Olsen, H. F. Smyth, G. E. Ferguson, and L. Scheflau (Ind. Eng. Chem. [Anal.], 1936, **8**, 260—263).—CCl_4 vapour in air (>10 p.p.m.) can be determined by passing the gas through a SiO_2 tube at 1000—1100° and absorbing the HCl produced in H_2O or NaOH. The R.H. of the air stream must be $\nless 70\%$ otherwise Cl_2 is formed. Absorption is facilitated by using a sintered glass disc and by adding EtOH (5%) or 1% of a 0·1% saponin solution to the absorbent. S. C.

Determination of volatile fatty acids by the partition method. O. L. Osburn, H. G. Wood, and C. H. Werkman (Ind. Eng. Chem. [Anal.], 1936, **8**, 270—275).—The method described previously (A., 1933, 933) has been applied to fermentation liquors containing AcOH, $EtCO_2H$, and $PrCO_2H$. Mixtures of two acids may be analysed by using one partition coeff. between H_2O and Et_2O; mixtures of three acids require two coeffs. Nomographic methods are used. HCO_2H is determined separately. S. C.

Reagent [mercuric chloride+sodium ethoxide] for determination of structure [of organic compounds]. R. Connor and J. H. Van Campen (J. Amer. Chem. Soc., 1936, **58**, 1131—1134).—Treatment of $CHR'R''\cdot COR$ and $CHRY\cdot CO_2R'$ (Y= labilising group; R=H, Alk, or Ar) dissolved in EtOH–NaOEt with EtOH–$HgCl_2$ gives a colourless (or nearly so) ppt. (+ test). The test is limited to neutral compounds containing C, H, and O only. The behaviour of >200 compounds is investigated. H. B.

Acidity determination in non-aqueous solutions. O. Tomiček and J. Feldmann (Časopis českoslov. Lék., 1935, **15**, 127—137; Chem. Zentr., 1935, ii, 2980).—Potentiometric titrations of $H_2C_2O_4$, BzOH, and salicylic acid in a wide range of solvents are described. A Te electrode (prep. described in detail) is useful in such titrations. H. N. R.

Differentiation between aldehydes and ketones. E. Graf (Anal. Fís. Quím., 1936, **34**, 91—94).—Ketoximes and aldoximes with nascent Cl (freshly prepared solution of $KMnO_4$ in dil. HCl) give respectively a bluish-green coloration due to chloronitroso-compounds, and chloro-oximino-compounds which give a red colour with $FeCl_3$. The reaction is not given by certain aromatic aldehydes. F. R. G.

Scheme for investigation of compounds containing the carbonyl group. E. Graf (Anal. Fís. Quím., 1936, **34**, 95—99).—The reaction between compounds containing ·CO· and NH_2OH,HCl is made the basis of a scheme for the recognition of acid chlorides, anhydrides, ketones, aldehydes, amides, esters, lactones, and org. acids (cf. Feigl, A., 1934, 790, and preceding abstract). F. R. G.

Analytical uses of Nessler's reagent. Determination of monosaccharides and disaccharides. Determination of furfuraldehyde. II. M. Goswami and B. C. Das-Purkaystha (J. Indian Chem. Soc., 1936, **13**, 315—322).—Arabinose (2), glucose (4), fructose (5), sucrose (9), lactose (5), and maltose (5) may be determined by adding K_2HgI_4 and Na_2CO_3, and dissolving the ppt. of Hg in excess of I, which is then determined volumetrically; for furfuraldehyde (2), Na_2CO_3 is replaced by NaOH. The figures in parenthesis indicate the no. of O atoms utilised by 2 mols. of the sugar for oxidation. The method may be used for blood-sugar. F. R. S.

Oxidation of amino-acids. Determination of the keto-acids and [detection of the] hydrogen peroxide produced. F. Bernheim, L. C. Bernheim, and A. G. Gillaspie (J. Biol. Chem., 1936, **114**, 657—663).—When *dl*-alanine, *l*-valine, *d*-serine, *d*-leucine, *l*-*iso*leucine, *d*-phenylalanine, *dl*-methionine, *dl*- or *l*-proline, or *d*-histidine is oxidised by purified kidney enzymes, 54—98% of keto-acids are formed [as detected by H sulphite compounds or 2 : 4-dinitrophenylhydrazones (I), which do not give identical results]. H_2O_2 is also formed, being detected by formation of methæmoglobin. (I) are determined by reaction with I (2 I consumed) and back-titration with $Na_2S_2O_3$. R. S. C.

Precision combustion of natural products. L. F. Fieser and R. P. Jacobsen (J. Amer. Chem. Soc., 1936, **58**, 943—947).—Baxter and Hale's method (this vol., 540) is adapted for use of about 1 g. of material. The following are analysed (the results agree with the theoretical vals. within about 0·02% for C and 0·01% for H): BzOH; $C_6H_3Ph_3$; dihydrocholesterol; dehydrodeoxycholic acid; chlorogenin, whence $C_{27}H_{44}O_4$ (cf. Liang and Noller, A., 1935, 673); sarsasapogenin, whence $C_{27}H_{44}O_3$ (cf. Simpson and Jacobs, *ibid.*, 864, 1248); fichtelite, whence $C_{19}H_{34}$ (cf. Ruzicka and Waldmann, *ibid.*, 741). H. B.

Determination of 5-methylfurfural[dehyde]. H. A. Iddles and K. S. French (Ind. Eng. Chem. [anal.], 1936, **8**, 283—285).—5-Methylfurfuraldehyde is quantitatively pptd. with either 2 : 4-dinitrophenylhydrazine or thiobarbituric acid. It may also be determined by pptn. with phloroglucinol if a factor is introduced for the solubility of the ppt. Absorption of Br is erratic (varies from 2 to 5 mols.) and the volumetric $KBrO_3$–KBr method is not therefore satisfactory. S. C.

Salting-out and salting-in microchemical reactions. B. V. J. Cuvelier (Natuurwetensch. Tijds., 1936, **18**, 73—74).—$ZnHg(SCN)_4$ is best prepared from $Zn(NO_3)_2$ and $NaHg(SCN)_3$. $(NH_4)_2SO_4$ is the best salt for salting-out nicotine. Antipyrine can be salted-out from H_2O solution with Na_2SO_4 or NaCl either in crystals, or in oily droplets. S. C.

Biochemistry.

Gaseous exchange in the human lung. I. Oxygen content and tension in arterial and venous blood. II. Equilibrium between oxygen tensions in alveoli and blood. K. Matthes. **III. Circulation and respiration during bodily work.** K. Matthes and W. Hauss. **IV. Gaseous exchange in the lungs during bodily work.** K. Matthes, M. Böhme, and K. Tietze (Arch. exp. Path. Pharm., 1936, **181**, 630—639, 640—654, 655—665, 666—673; cf. this vol., 91).—I. The degree of O_2 saturation of a few drops of blood (from the capillaries) is determined photometrically, using a modified form of Kramer's apparatus (A., 1935, 371). Changes in the amount of light transmitted through the ear (after injection of histamine) registered by means of a photo-electric cell are a logarithmic function of the degree of arterial O_2 saturation. When other vals. for arterial and venous blood are determined and calc. all the essential factors determining gaseous exchange in the lungs are known. The resting and (moderate) working vals. for degree of O_2 saturation and tension of venous blood are 66 and 52% and 35 and 29 mm. of Hg respectively.

II. The difference between the O_2 tensions in alveoli and blood when the inspired air has reduced $[O_2]$ is $<$ the val. calc. on the basis of the theory of incomplete equilibrium. This may be due to increase in the no. of all the alveolar capillaries.

III. The increased diffusion const. of gaseous exchange in the lungs during moderate exercise is explained similarly.

IV. Little reduction in the difference between the O_2 tensions in alveoli and blood is caused by inspiring air of reduced O_2 content when bodily work is performed and the rule of incomplete equilibrium holds apparently because the increase in the no. of alveolar capillaries reaches its limit as a result of the work alone. W. McC.

Effect of the composition of inspired air on the circulation through the brain. L. Irving and M. S. Welch (Quart. J. Exp. Physiol., 1935, **25**, 121—129).—Inhalation of 10% CO_2 in O_2 increased the blood-flow in the brain but decreased that in the hind leg. Alveolar O_2 deficiency did not cause these changes. The CO_2 pressure changed more rapidly in brain than in the leg. Ch. Abs. (*p*)

Reflex regulation of respiration from the carotid sinus. G. Stella (Quart. J. Exp. Physiol., 1935, **25**, 145—153).—Effects were more marked during respiration in air than in an atm. containing CO_2 (3—5%) and air. Ch. Abs. (*p*)

Breath odours from alliaceous substance. Cause and remedy. H. W. Haggard and L. A. Greenberg (J. Amer. Med. Assoc., 1935, **104**, 2160—2163).—Odour comes entirely from particles of garlic or onions retained in the mouth. Expired air showed 0·0028—0·0035 mg. of diallyl sulphide per litre. Rinsing with 3% NH_2Cl destroyed all odour. Ch. Abs. (*p*)

Oxygen dissociation curve of hæmoglobin in dilute solution. R. Hill and H. P. Wolvekamp (Proc. Roy. Soc., 1936, B, **120**, 484—495).—Dil. suspensions of human blood corpuscles and whole blood show similar O_2-dissociation curves, but dil. solutions of human hæmoglobin have a three-fold increased affinity for O_2. The blood of other animals shows similar effects, to varying extents. F. A. A.

Gaseous nitrogen content of the blood. G. Leiner (Z. klin. Med., 1935, **128**, 560—567; Chem. Zentr., 1935, ii, 2837).—The mean normal N_2 content is 1·2 vol.-%. It is increased in severe emphysema, bronchitis, and hypoxæmia. R. N. C.

Formation of hæmatoidin *in vitro* from mammalian erythrocytes. J. S. F. Niven (J. Path. Bact., 1935, **41**, 183—197).—Cryst. hæmatoidin was formed within macrophages from added erythrocytes in cultures of mammalian tissues. In some cases a diffuse yellow pigment, giving a diffuse Fe reaction, preceded the appearance of formed pigment. Ch. Abs. (*p*)

Local formation of blood-pigments. R. Muir and J. S. F. Niven (J. Path. Bact., 1935, **41**, 183—197).—In mice and rats formation of granular and cryst. pigment from subcutaneously injected erythrocytes is intracellular. Phagocytosis of erythrocytes is followed by production of diffuse and granular forms of hæmosiderin. Hæmatoidin (I) is formed subsequently (cf. preceding abstract). Similar effects are produced by injection of hæmoglobin. (I) is not produced in rabbits by this treatment. Ch. Abs. (*p*)

Delicate test for blood-pigments. C. B. Jensen and W. M. Urbain (Food Res., 1936, **1**, 275—276).—The pigment is converted into nitrosohæmoglobin or nitrosohæmochromogen and then, by treatment with H_2O_2, into a green compound. E. C. S.

Derivatives of blood-pigments.—See this vol., 1129.

Ultra-violet spectrum of normal and leucæmic blood. I. Magat and M. Magat (Compt. rend., 1936, **202**, 2181—2184).—The ultra-violet absorption curve of the blood of leucæmic fowls lies slightly above that of the normal fowl between 200 and 450 mμ, especially between 240 and 290 mμ. Absorption bands at 411, 343, 280, and 240 mμ found by Suhrmann and Kollath (A., 1927, 688) are confirmed: a further max. occurs at 289·5 mμ (possibly due to material accompanying cancerous growths). F. N. W.

Absorption spectra of some modified snake venoms. H. F. Holden (Austral. J. Exp. Biol., 1936, **14**, 121—130).—The hæmolysins were fairly resistant to dil. acid at 60° and very little change in the absorption spectra was observed, even when most of the hæmolysin was inactivated. In alkaline solution, inactivation was rapid and the absorption bands were rapidly obliterated. With CH_2O the hæmolysins were inactivated but changes in the spectra were irregular. H. G. R.

Blood-sugar of the bee (*Apis mellifica*). R. Beutler (Naturwiss., 1936, **24**, 486—491).—The blood-sugar of bees varies from 0 to 4% (and in a few cases up to 7%; average 2%), is partly fermentable, and, together with the high serum-P, is probably related to muscular activity of flight. F. O. H.

Glycerol content of the organism. E. Trabucchi (Boll. Soc. ital. Biol. sperim., 1932, 7, 916—921).—The glycerol (I) content of the blood of rabbits after injection $\propto$ the amount of (I) injected, and is related to the amount fixed in the organs; the last two are independent of one another. The amount of (I) recoverable from the blood 5 min. after injection often reaches double the amount calc. on the basis of a uniform distribution throughout the organism. The concn. curve of (I) does not fall below this val., but stabilises itself. Injection of insulin immediately following (I) causes a fall of blood-(I). R. N. C.

Protein and urea in the blood of rabbits infected with *Trypanosoma annamense*. H. Launoy and H. Lagodsky (Compt. rend. Soc. Biol., 1936, 122, 1055—1058).—During the first 15 days the albumin : globulin ratio decreased, there being an increase in globulin and a decrease in albumin. Total and urea-N do not vary, but hypercholesterolæmia occurs. H. G. R.

Blood [changes in anæmia and other diseases]. R. Isaacs, C. C. Sturgis, F. H. Bethell, and S. M. Goldhamer (Arch. Int. Med., 1936, 57, 1186—1246).—A review of recent literature. E. D. Y.

Extracting morphine from organ tissues, especially blood. F. Suzuki (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharm. Soc., 1933, 50—51).—The sample is incubated with papain, digested with 0·2 vol. of EtOH, and repeatedly shaken with $CHCl_3$. Morphine in the $CHCl_3$ extract is adsorbed on fuller's earth, re-extracted with $CHCl_3$, and titrated by Gordin's method with alizarin-red. Ch. Abs. (*p*)

Two mechanisms for the formation of hexose diphosphate from glucose in intact human erythrocytes. Z. Dische (Naturwiss., 1936, 24, 462).—Phosphorylation of glucose in erythrocytes takes place by the transference of PO_4''' from adenosinetriphosphoric acid. In erythrocytes kept at 0° for some time, a second method involving intermediate formation of adenosinediphosphoric acid occurs. The latter process only is prevented by 0·004*N*-$CH_2I{\cdot}CO_2H$. A. L.

Transfer of inorganic phosphorus across the red blood-cell membrane. L. Halpern (J. Biol. Chem., 1936, 114, 747—770).—In 29 out of 33 analyses of inorg. P in red blood cells and in serum, more inorg. P was present per unit of H_2O in serum than in cells, the differences ranging from 0·42 to 9·81 mg. per 100 c.c. of H_2O. At 3° there was no diffusion of inorg. P across the cells, and at 23° the process was very slow, but at 37·5° there was a large increase in diffusion, possibly related to the metabolism of glucose in the cell rather than to the temp. When carbohydrate metabolism *in vivo* was accelerated by injection of glucose and insulin, the concn. of inorg. P in cells and serum decreased. Addition of glucose and NaF *in vitro* at incubator temp. caused inorg. P to enter the cell during glycolysis, but this diffused out again when glycolysis was complete even though the concn. in the serum was already $>$ that in the cells. The simple laws of diffusion cannot explain the transfer of inorg. P, which seems to depend mainly on the metabolic processes in the cell. J. N. A.

Oligolytic concentrations of saline with respect to the erythrocytes of the blood of various animal species. S. Matuzaki (Keijo J. Med., 1936, 7, 113—155).—Hæmolysis curves and oligolytic concns. were determined. The curves are sp. for each species, but there is a similarity between those of related species. J. N. A.

Somatic phenomenon of the weaning of children with respect to the water content of the blood. T. Ryô (Keijo J. Med., 1936, 7, 1—19).—Methods for determining H_2O content are discussed, and that of Kuroda (A., 1933, 1094) is recommended. The amount of H_2O decreases with age, but there is a sharp rise in H_2O content in boys from 250 to 400 days, and in girls from 400 to 500 days old, and then a decrease, corresponding with the period of weaning. In animals the H_2O content is high at birth, then falls to a lower level, and then rises at weaning and falls again, whilst with children the H_2O content is rather less at birth, and there is not the preliminary fall before weaning. J. N. A.

Content of bromine in blood. G. Moruzzi and P. Guareschi (Arch. Ist. Biochim. Ital., 1936, 8, 229—248).—Br' is determined in presence of I' and high [Cl'] by a modified Palmer–Clarke method (A., 1933, 312) with an error of approx. 2×10^{-5} g. Blood-Br of man and various animals is $35\pm25\times10^{-5}$%. Approx. 40—80% of serum-Br is diffusible, whilst the distribution of Br between serum and corpuscles is uniform relative to their H_2O content. F. O. H.

Blood-forming action of copper. G. Dolfini and S. Casuccio (Rass. Clin. Terap., 1933, 32, 291—318; Chem. Zentr., 1935, ii, 2837). R. N. C.

Blood-iodine in clinical practice. E. P. McCullagh and D. R. McCullagh (Arch. Int. Med., 1936, 57, 1061—1066). E. D. Y.

Influence of diuretics on the alkali reserve of blood. G. Gottsegen (Wien. klin. Woch., 1935, 48, 1116—1118; Chem. Zentr., 1935, ii, 2840).—In general, the alkali reserve is increased by diuretics. H. N. R.

Effect of bleeding on distribution of ions between erythrocytes and plasma in health and in hypertony and nephritis. I. F. Schmitt and W. Basse (Arch. exp. Path. Pharm., 1936, 181, 584—597).—Removal of 500 c.c. of venous blood causes reduction (followed, in healthy persons, by a rise above the initial val.) in the CO_2-binding capacity of the blood in healthy and diseased persons. [Cl'], [Na·], and [K·] fall in the erythrocytes and rise in the plasma, but the increase in the plasma is only partly at the expense of the erythrocytes. [Ca··] rises in the plasma and erythrocytes. The effects in disease are $<$ in health. W. McC.

Porphyrin in the serum of fœtuses and newborn children. R. Fikentscher (Klin. Woch., 1935, 14, 569—571).—The sera contain an Et_2O-sol. porphyrin spectroscopically different from protoporphyrin, and resembling most closely coproporphyrin. It is not present in the maternal serum.

R. N. C.

Blood-serum-lipins in cancer and other cases. I. Mean mol. wt. of the free and combined acids. H. H. Barber. **II. Ultra-violet absorption measurements.** L. A. Woodward (Biochem. J., 1936, **30**, 1463—1467, 1467—1471).—I. No variation was observed in the sap. val. of the serum-lipins of normal and cancerous blood.

II. The shape of the absorption curve of an extract from blood-serum cannot be used as a diagnostic test for cancer. H. G. R.

Alexic properties of protein-*C*. M. Doladilhe and M. Michel (Compt. rend., 1936, **202**, 1950—1952; cf. this vol., 875).—The capacity for hæmolysis possessed by alexic guinea-pig or human serum is enhanced or diminished as the concn. of protein-*C* derived from a foreign or homologous serum is increased. The effect is complementary when *C* is derived from fresh serum, but if *C* is heated for 15 min. at 57°, it is without effect on the hæmolysis. Serum deprived of its globulins (cf. this vol., 495) has no hæmolytic power until fresh *C* is added and is the greater the more *C* is present. J. L. D.

Modifications in the protein fractions of serum during periods of rest and crisis in anaphylaxis. Aubry, Thiodet, and Ribère (Compt. rend. Soc. Biol., 1936, **122**, 947—950).—In a crisis the equilibrium is normal or low and is increased during periods of rest. H. G. R.

Hæmolysis and cholesterologenesis. V. de Lavergne and P. Kissel (Ann. Inst. Pasteur, 1936, **57**, 56—78).—The hypercholesterolaemia produced by inoculation with hæmolytic bacteria can be simulated by the use of saponin and solanine, if the surrounding medium is not sufficiently acid to ppt. the cholesterol. P. G. M.

Mechanism of hæmolysis from the point of view of active mass in heterogeneous systems. H. Nakamura and K. Kuroda (Keijo J. Med., 1936, **7**, 20—97).—The active mass in the hæmolytic system can be distinguished from that in the ordinary heterogeneous system, for in the erythrocyte the system is not only heterogeneous, but is restricted by the cell wall. The "mechanical active mass," the kinetic active mass given to erythrocytes by mechanical agitation, is an important factor in hæmolysis. With const. temp., proportion of erythrocytes, and "mechanical active mass," the degree of hæmolysis is high in dil. saline; increase of [NaCl] causes a sudden fall to a min. val., and then, as the concn. increases, it slowly rises again. The concn. for min. hæmolysis differs markedly from the isotonic concn. and is 1—2% NaCl for ox, and 3% for hen, erythrocytes. It is called the "oligolytic concn.," and is sp. for each animal species. If the "mechanical active mass" be taken into account, hæmolysis occurs in isotonic saline, as well as in more conc. solutions. Washing erythrocytes with isotonic saline affects cell resistance. High and low temp. accelerate hæmolysis, but a medium temp. is almost without effect, and that temp. which causes a min. hæmolysis is called the "oligolytic temp." Hæmolysis instantly reaches a max. when erythrocytes are placed in hypo-oligolytic saline, whilst action is very slow in iso- or hyper-oligolytic solutions. The η of the system retards hæmolysis because it diminishes the mechanical active mass. Hæmolysis increases with an increase of erythrocytes up to a certain val., but it decreases with high concns. of erythrocytes. J. N. A.

Classical theory of blood coagulation and its modern development. E. Wöhlisch (Naturwiss., 1936, **24**, 513—517).—A review.

Clotting of blood and milk. I. Physical and chemical influences. M. F. von Dungern and G. Nelz (Z. Biol., 1936, **97**, 277—296).—The clotting times of (human) blood (t_1) and (cow's) milk (t_2) are logarithmically related to the temp. Removal of CO_2 in a vac. lowers t_1 to 3·5 min. at 25°, but does not affect t_2, whilst saturation with CO_2 raises t_1 to 6 min. but diminishes t_2; air, O_2, N_2O, and coal gas have no effect on either t_1 or t_2. The vals. of t_1 and t_2 vary considerably according to the nature of the interface, those with glass and quartz (which are more easily wetted) being $<$ those with paraffin wax etc. P. G. M.

Anti-complex of fibrin. S. S. Perov (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1934, No. 6, 3—22).—Blood-fibrin consists of the proto-acid (this vol., 1037), combined with another protein, the "anticomplex." Isolation of the latter is described. In 1% solution, unlike the complex (fibrinic acid), it has very low η. Ch. Abs. (*p*)

Tests for innocuity and antigenic potency of staphylococcus toxoid. C. E. Dolman and J. S. Kitching (J. Path. Bact., 1935, **41**, 137—162).—Standardisation and formalinisation of toxins are examined. Ch. Abs. (*p*)

Haptens and inhibition of the hæmolytic power of certain immuno-sera. R. D. de la Rivière, N. Kossovitch, and S. Ishii (Compt. rend. Soc. Biol., 1936, **122**, 1045—1048).—Inoculation with hapten results in formation of the corresponding antibody only if protein is injected at the same time.

H. G. R.

Nature of the tubercular antibody. Existence of protein–fat antibodies. K. Meyer (Compt. rend. Soc. Biol., 1936, **122**, 1037—1038).—In certain anti-tubercular sera, antibodies which react equally well with the protein- or fat-antigen of *B. tuberculosis* are present. H. G. R.

Size of antibodies. J. Biscoe, F. Herčík, and R. W. G. Wyckoff (Science, 1936, **83**, 602—603).—The sedimentation consts. of several conc. antibody preps. are of the same order of magnitude as those of the globulins of normal sera. Antibody properties are not necessarily associated with exceptionally large mol. size. L. S. T.

Purification of antibodies in type I antipneumococcus serum; nature of the type-specific precipitin reaction. B. F. Chow and W. F. Goebel (J. Exp. Med., 1935, **62**, 179—202).—Fractionation of the antibody protein by $(NH_4)_2SO_4$

and dialysis yields a relatively inert euglobin and an active pseudoglobulin. The immune globulin contains 14·85% N; the antibody protein has approx. 2·75% of lipin and a prosthetic carbohydrate grouping. The distribution of basic NH_2-acids in globulins of normal and immune horse serum is similar except for a slight difference in lysine content. Replacement of one H in the primary NH_2 by Ac largely decreases the capacity of the immune protein to ppt. the type-sp. polysaccharide. The specificity of the antibody protein is lost on treatment with CH_2O. Esterification shows the CO_2H to be of primary importance in rendering the type I polysaccharide serologically reactive; replacement of the NH_2 or OH has a less pronounced effect. CH. ABS. (*p*)

Ultracentrifugal and electrophoretic studies on antibodies. M. HEIDELBERGER, K. O. PEDERSEN, and A. TISELIUS (Nature, 1936, **138**, 165).—A horse-serum prep. of type I pneumococcus anti-carbohydrate showed almost homogeneous sedimentation with the const. $S_{20}=17{\cdot}2\times10^{-13}$. The electrophoresis was homogeneous with an isoelectric point at p_H 4·8. With horse antibodies the antibody function is connected with a heavy, and otherwise minor, component. With rabbit sera homogeneous sedimentation was obtained with no appreciable difference between the consts. of the globulin fractions of normal serum and immune serum, or of normal globulin and immune globulin containing up to 50% of anti-ovalbumin, or antibody to type III pneumococcus polysaccharide containing 90% of precipitin. The rabbit appears to produce antibody from the principal globulin component. L. S. T.

Auto-antibody production for bone-marrow. V. BURKE, C. F. BRADLEY and N. P. SULLIVAN (Res. Stud. State Coll. Washington, 1935, **3**, 1—11).—Complement-binding iso- and auto-antibodies develop in rabbits following injection of rabbit bone-marrow antigen. Changes in the blood picture resemble anæmia and are less marked after subsequent injections. Anti-bone-marrow serum is non-hæmolytic. Auto-agglutinins active at room temp. occur in some rabbits after bone-marrow injections. A. G. P.

Hydrogen-ion concentration of Hortega cells. S. TAKEUCHI (Z. Klin. Path. Hämatol. [Japan], 1933, **2**, 341).—Vals. obtained were very close to those of reticulo-endothelial cells and differed from those of oligodendroglia and astrocytes. CH. ABS. (*p*)

Iodometric determination of small amounts of morphine in viscera. S. IKESHIMA (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharm. Soc., 1933, 51—52).—With 0·005*N*-I morphine (I) gives a const. ppt. [1 mol. of (I) with 2·55 atoms of I]. By this means 1 mg. of (I) is determined with an accuracy of 90%. CH. ABS. (*p*)

Nitroprusside reaction as a test for reduced glutathione. N. S. R. MALOEUF (Nature, 1936, **138**, 75—76).—This test is sp. for reduced glutathione in normal living tissues when aq. NH_3 is used as the alkali and no heat is applied. L. S. T.

Microscopy of powdered, desiccated endocrine glands. P. A. MATTIS (Amer. J. Pharm., 1936, **108**, 276—302).—Methods for the identification of characteristic histological elements in powdered ovary, corpus luteum, thyroid, and pituitary preps. are described. F. O. H.

Unsaponifiable matter of chrysalis oil. J. OZAKI and B. KASAI (J. Agric. Chem. Soc. Japan, 1936, **12**, 425—456).—Chrysalis oil from *Bombyx mori* contains 2·93% of unsaponifiable matter which consists of 18·07% of hydrocarbons ($C_{22}H_{46}$, $C_{24}H_{50}$, $C_{26}H_{54}$, and $C_{28}H_{58}$) and 81·93% of sterols (cholesterol and sitosterol). J. N. A.

Chemistry of insects. II. Woolly aphis and white pine chermes. B. K. BLOUNT (J.C.S., 1936, 1034—1036).—The woolly aphis, *Eriosoma lanigerum*, Hausmann, gives a wax and a cryst. orange pigment, *lanigerin* (I), $C_{17}H_{14}O_5$, with 3 active H. (I) is probably a substituted polyhydroxyanthraquinone. The white pine chermes, *Adelges* (*Pineus*) *strobi*, Börner, affords in addition to a *wax*, m.p. 106·1—106·4°, a dark purple-brown pigment, *strobinin* (II), $C_{30}H_{24}O_8$, with 3 active H. (II) gives the colour reactions of a substituted 2-hydroxyphenanthraquinone. J. H. B.

Coccids produced in Japan. IX. Carbohydrates and waxy substances of *Icerya purchasi*, Mask. M. KONO and R. MARUYAMA (J. Agric. Chem. Soc. Japan, 1933, **11**, 647—658).—The insect contained lignin 10·7, cellulose 0·7, pentosan 0·9, and mannan 1·9%. *l*-Arabinose was present in aq. extracts. C_6H_6 extracts yield a wax (d^{15} 0·914, m.p. 78°, sap. val. 157·5) of which ceryl alcohol, cerotic and palmitic acids and a resin acid, $C_{10}H_{16}O_4$, were the principal constituents, together with 31% of unsaponifiable matter. CH. ABS. (*p*)

Growth and water content of the bones of newly born pups and kittens. C. M. BURNS and N. HENDERSON (Biochem. J., 1936, **30**, 1202—1206).—The H_2O content of very young bone, which depends mainly on the size and H_2O content of the epiphysis and marrow cavity, increases in the long bones shortly after birth chiefly because of increase in the H_2O content of the diaphysis. The H_2O contents of the femora, humeri, and tibiæ exhibit no consistent differences. W. McC.

Mineral constituents of bone. II. Effect of age on mineral constituents of bones from kittens and pups. C. M. BURNS and N. HENDERSON (Biochem. J., 1936, **30**, 1207—1214; cf. A., 1935, 1396).—The salt content of the diaphysis (especially cancellous tissue) decreases immediately after birth. Later, the Ca content of the cortex increases slowly whilst that of the cancellous tissue remains low in the kitten and increases slowly in the pup. In temporary tissues (*e.g.*, calcified cartilage) the ratio CO_3''/Ca is low but it increases in tissues which are more slowly destroyed. In the bones of the adult dog and cat the ratio approaches that in dahlite. W. McC.

***apo*Cholic and dehydro*apo*cholic acid.** D. ADLERSBERG and B. LUSTIG (Arch. exp. Path. Pharm., 1936, **181**, 610—616).—Compared with *apo*cholic acid, dehydro*apo*cholic acid has less reducing effect on the surface tension of H_2O, less hæmolytic action, and lower toxicity but it has greater stimulating effect on bile secretion. Hence dehydrogenation of bile acids leads to reduction of toxicity and increased stimulating effect on bile secretion. W. McC.

Nucleic acids of the pancreas. II. *allo*-Nucleic acid. H. Steudel (Z. physiol. Chem., 1936, **241**, 84—92; cf. A., 1935, 646).—*allo*Nucleic acid (I), the chief nucleic acid of the nucleoprotein (II) of the pancreas, contains guanylic (III) and adenylic acid in the ratio 4 : 1, cytosylic and possibly uracylic acid. (III) is eliminated from (II) by alkaline hydrolysis, which also removes one half of (III) from (I) more easily than the other. Partly purified (I) (P : N ratio of Cu salt 1 : 1·9) is obtained from (II) by treatment with $Ba(OAc)_2$ followed by pptn. with $Cu(OAc)_2$. W. McC.

Crystalline substances from the adrenal gland.—See this vol., 1117.

***X*-Ray analyses of keratins.** A. Giroud and G. Champetier (Bull. Soc. Chim. biol., 1936, **18**, 656—664).—The mucous body of malpighi (the epidermis giving rise to keratins) and several schizokeratins and sclerokeratins give the same *X*-ray diagram, indicating that they all possess the α-keratin structure. The longitudinal unit spacing of the polypeptide skeleton is therefore unchanged during the process of keratin formation. A. L.

Constituents of unsaponifiable matter of sperm blubber oil.—See this vol., 1091.

Absorption spectrum of bilirubin.—See this vol., 1048.

Absorption spectra of cerebrospinal fluid. M. Païc (Compt. rend. Soc. Biol., 1936, **122**, 1029—1031).—The course of the absorption curve and the optical density of the max. (280 mμ) $\propto$ the protein content. No difference was observed between serologically positive or negative fluids. H. G. R.

Histospectrography of the corneal ring of Kayser and Fleischer. A. Policard, P. Bonnet, and G. Bonamour (Compt. rend. Soc. Biol., 1936, **122**, 1120—1122).—Traces of Cu in the region of the ring only were found; Ag, Fe, and Zn were absent. H. G. R.

Action of alkaline persulphate on amino-acids. K. Lang (Z. physiol. Chem., 1936, **241**, 68—70).—NH_3, frequently in almost theoretical yield, is eliminated from NH_2-acids by boiling with alkaline aq. $K_2S_2O_8$. With aliphatic $(NH_2)_1$-acids CO_2 is also eliminated and the corresponding aldehydes are produced in yields which are poor but increase as the mol. wt. of the acid increases. With monoaminodicarboxylic acids, serine, and cystine extensive decomp. accompanies NH_3 liberation. With diaminomonocarboxylic acids and arginine >1 but <2 mols. of NH_3 are liberated and with phenylalanine, tyrosine, and tryptophan the NH_3 yields are $<$ theoretical. Proline loses CO_2 and yields an unstable *pyrroline* (*reineckate*, m.p. 195—210°). Alkaline $K_2S_2O_8$ also attacks urea, creatine, and creatinine, with liberation of $<$ the theoretical amount of NH_3. W. McC.

Effect of denaturation on colloidal behaviour of ovalbumin.—See this vol., 1068.

Spreading properties of azoproteins in the dermis. A. Claude (J. Exp. Med., 1935, **62**, 229—244).—The spreading property of azoproteins when introduced intradermally is not specifically influenced by the aromatic component or the type of protein but is derived from the presence of the azo-group. It is controlled by the no. of diazo-groups in the protein mol. and $\propto$ the concn. of the solution. Azo-compounds of low mol. wt. have no significant effect on skin permeability. Ch. Abs. (*p*)

Mechanism of coagulation of proteins by tannic acid. S. S. Perov (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1935, No. 7, 26—38).—Tannic acid (I) ppts. protein, not by chemical combination with it but by increasing the $[H^{\bullet}]$ to approach the isoelectric point. (I) may be adsorbed by pptd. protein. Ch. Abs. (*p*)

Glucoproteins. II. Polysaccharides of vitreous humour and of umbilical cord. K. Meyer and J. W. Palmer [with E. M. Smyth] (J. Biol. Chem., 1936, **114**, 689—703; cf. A., 1935, 232).—Hyaluronic acid (I), from vitreous humour, is obtained substantially free from N-contaminants by means of $Zn(OH)_2$; hydrolysis gives 1 mol. each of glucosamine and (?) glycuronic acid. Aq. extraction of umbilical cord gives a substance similar to (I) (probably derived from Wharton's jelly), and alkaline extraction of the residue gives a sulphuric ester (probably derived from the connective tissue) which yields chondrosamine. The viscosity of polyuronic acids depends on their source and treatment. Artificial mucoids are obtained from polyuronic acids and proteins. R. S. C.

Nitrogen and phosphorus compounds of the muscles of thyroidectomised animals. E. Kratinova (Ukrain. Biochem. J., 1932, **5**, 58—70).—In the muscles of thyroidectomised rabbits and dogs, the H_2O content was definitely and the creatine content but slightly increased, the creatinephosphoric acid was markedly decreased, whilst the residual N underwent no regular change. W. O. K.

Oxygen dissociation curves of muscle-hæmoglobin. R. Hill (Proc. Roy. Soc., 1936, B, **120**, 472—483).—Dissociation curves, determined spectroscopically, of heart muscle-hæmoglobin (I) of ox, sheep, dog, and goose differ from those of blood-(I) in being hyperbolic and depending little on p_H, as recently found for horse heart muscle-(I) (Millikan, this vol., 1012). Muscle-(I) has a much higher O_2 affinity than blood-(I). The physiological function of muscle-(I) is discussed. F. A. A.

Creatine derivatives. I. Presence of creatinine in muscular tissue. II. Supposed creatine of the residue of nervous and muscular tissues extracted with acids. I. Ciaccio (Boll. Soc. ital. Biol. sperim., 1934, **9**, 227—229, 229—231).—I. Extracts of frog muscle give a positive Jaffé reaction, which, however, is not sp. for creatinine.

II. The residue always gives a positive Jaffé reaction, the substance responsible, determined as creatine (I), representing approx. 1/3 of the amount of (I) extracted by $CCl_3{\cdot}CO_2H$. It probably originates from the hydrolysis of acid-insol. protein-like material;

the amount is increased by heating for 2 hr. It is not adsorbed on kaolin, and is therefore not (I).
R. N. C.

Cholesterol content of muscle. W. R. Bloor (J. Biol. Chem., 1936, **114**, 639—648; cf. A., 1935, 109).—The cholesterol (I) contents of the different types of muscle were sharply differentiated and in the order: unstriped $>$ cardiac $>$ striped; it is suggested that a high phospholipin content, as in striped muscle, is associated with muscular activity and a high (I) content, as in unstriped muscle, with a more extensive nerve supply. H. D.

Rapid production of cholesterol from brain. I. Remesov and N. Levaschova (Z. physiol. Chem., 1936, **241**, 81—83).—Pure cholesterol (I) in 83% yield is obtained in 24 hr. by grinding 1 kg. of pulped brain in portions for 3—4 hr. with 4·5 vols. of liquid air, shaking the moist powder thus obtained twice with 2·5-litre portions of cold anhyd. COMe$_2$, filtering, evaporating the solvent under reduced pressure, and crystallising the residue from EtOH–Et$_2$O. A further amount of crude (I) is obtained by extracting the dried residue from the COMe$_2$ treatment with hot COMe$_2$. W. McC.

Milk sera for refractometric studies. R. Turnau (Oesterr. Chem.-Ztg., 1936, **39**, 121—124).—The refractive properties of two CCl$_4$ sera of milk containing milk 50 c.c., CCl$_4$ 5 c.c., and 20% AcOH 1 c.c., one being prepared from heated (20 min. at 100°) and subsequently cooled milk, are described. The heated milk serum shows the same n as Cu, Pb, and Ca acetate sera. W. L. D.

Determination of urine in milk. L. Buruiana (Lait, 1936, **16**, 698—705).—Normal cow's urine [0·26% creatinine (I) content] contains 120 times as much (I) as does milk. The serum obtained by CaO–Cu pptn. of the milk-proteins uniformly contains 35% of the (I) of the milk. (I) in the serum is determined photometrically by the picrate method, which detects 1% of urine. W. L. D.

Differential reactions of human and cows' milk. II. M. Polonovski and F. Moreno Martín (Anal. Fís. Quím., 1935, **33**, 887—904; cf. A., 1935, 1267).—Three new methods are proposed to determine the amount of cows' milk or H$_2$O added to human milk. (*a*) 1 c.c. of milk is neutralised (phenolphthalein with 0·01N-NaOH, and the "buffer index" (c.c. of 0·01N-H$_2$SO$_4$ required for neutralisation in presence of Me-orange) is determined. This index varies with composition, from 2·5 for cows' to 10 for human milk. (*b*) 0·1 g. of the butter is saponified and distilled. The "volatile acid index" (c.c. of 0·01N-NaOH required to neutralise the acids using phenolphthalein) $\propto$ the composition, from 0·3 for human to 6·5 for cows' milk. This method cannot give accurate vals. with separated milks. (*c*) Total carbohydrates, determined by the dichromate method of Polonovski *et al.* (A., 1931, 251), $\propto$ the composition from 5 g. for cows' to 8 g. per litre for human milk.
F. R. G.

Nitrogenous constituents of milk and their separate determination in human milk. F. Moreno Martín (Anal. Fís. Quím., 1935, **33**, 905—930).—In 2 c.c. of human milk total N is determined by the micro-Kjeldahl method, casein by pptn. with NaOAc and AcOH at p_{H} 4·2, and albumin by pptn. with tannic acid. F. R. G.

Heat-coagulation of caseinogen. II. Rate of phosphorus cleavage. G. R. Howat and N. C. Wright (Biochem. J., 1936, **30**, 1413—1415; cf. A., 1934, 1119).—When aq. solutions of Ca caseinogenate were heated at 90—115° for 1—45 hr. the degree of coagulation varied directly with the liberation of acid-sol. P; Q_{10} was approx. 3. H. D.

Agglutinins in human milk. S. Amagasa (Z. Klin. Path. Hämatol. [Japan], 1932, **1**, 99).—Colostrum, ripe milk, and final milk each contains one of the corresponding blood-group agglutinins. Colostrum and final milk have higher agglutination titres than has blood serum, and frequently show a non-sp. group agglutination. Ch. Abs. (*p*)

Disturbing colorations in the lactic acid limit reaction for the stomach content. G. Sant (Pharm. Tijds. Nederl.-Indië, 1935, **12**, 223; Chem. Zentr., 1935, ii, 2854).—Addition of 3% H$_2$O$_2$ prevents disturbing side-colorations.
H. N. R.

Effect of Schiff's zwieback on secretion of gastric glands. S. D. Frumin (Problems of Nutrition [Russia], 1933, **2**, No. 3, 56—60).—Administration of zwieback to dogs is followed by a type of gastric secretion intermediate between those produced by a meat and a bread diet. The amount and acidity of the secretion are greater when the dry product is used. Continuous feeding lowers the secretory function in 6 days. Ch. Abs. (*p*)

Influence of soya beans on gastric secretion. A. R. Striganova (Problems of Nutrition [Russia], 1933, **2**, No. 4, 33—44).—The effect of soya-bean diet on gastric secretion is intermediate in character between those of bread and of meat diets. Soya-bean protein may serve, to some extent, as a substitute for meat protein. Ch. Abs. (*p*)

Effect of hydrolysates of casein and those from the intestine on the secretion of gastric glands. P. N. Kurdjumov (Problems of Nutrition [Russia], 1933, **2**, No. 5, 61—68).—Addition of the hydrolysate to a bread and H$_2$O diet for dogs increased gastric secretion. The latter was lowered by additions of milk and not appreciably affected by additions of meat. Ch. Abs. (*p*)

Reactions of the contents of the jejunum and experimental production of peptic ulcer. P. P. T. Wu (Arch. Surg., 1935, **30**, 557—562).
Ch. Abs. (*p*)

Determination of the hydrogen-ion concentration of the intestinal juice of the larvæ of clothes- and wax-moths by means of the glass electrode. F. Duspiva (Z. physiol. Chem., 1936, **241**, 168—176).—The p_{H} of a few drops of the juice (also of alkaline liquids in absence of CO$_2$ and suspensions) is determined with a special type of glass electrode. The average p_{H} of juice from clothes- and wax-moths are 9·9 and 8·4, respectively. The val. is probably not affected by the quality of the food consumed.
W. McC.

Origin of choline in semen. E. Kahane and J. Lévy (Compt. rend., 1936, **202**, 2186—2188).—The existence of free choline in semen is due to the action of an enzyme on a precursor. F. N. W.

Urinary ammonia. S. Mikaéloff (Bull. Soc. chim., 1936, [v], **3**, 1048—1052).—The results of standard methods of determination are compared. The advantages of Sahli's method are discussed. E. S. H.

Determination of meconic acid in urine of opium addicts. I. S. To and K. Yo (Japan. J. Med. Sci., IV, No. 1; Proc. Japan. Pharm. Soc., 1933, 6—9).—The sample is made alkaline with NaOH, treated with $CaCl_2$, filtered after 1 hr., and the ppt. dissolved in AcOH. A few drops of dil. HCl are added together with $FeCl_3$. The intensity of the red colour is measured. Samples showing colour with HCl but no $FeCl_3$ are discarded. Tests on opium addicts are recorded. Positive reactions are obtained in most cases. Non-addicts all showed negative tests. Administration of meconic acid to man and animals caused a positive test in urine for 1—3 days. Ch. Abs. (*p*)

Determination of morphine in urine of opium and of morphine addicts: practical application of the reaction. S. To and A. Rin (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharm. Soc., 1933, 11—15).—The acidified (HCl) urine is conc., filtered, made alkaline with aq. NH_3, and extracted with $CHCl_3$. After evaporation of the $CHCl_3$ the residue is dissolved in aq. NH_3 and morphine (I) is extracted with H_2SO_4. After further treatment with aq. NH_3, (I) is extracted by $CHCl_3$ and determined by customary methods. (I) is eliminated in urine of opium and (I) addicts. Applied in conjunction with the meconic acid test (preceding abstract) the test serves to distinguish the two classes of addicts. Ch. Abs. (*p*)

Acetoacetic acid in urine. Constitution of the coloured compounds formed in the reaction of acetoacetic acid and its ester with sodium nitroprusside in presence of ammonia (with or without ammonium sulphate) and certain amines. F. E. Raurich Sas (Anal. Fís. Quím., 1935, **33**, 247—278).—The use of Lange's test for $CH_2Ac\cdot CO_2H$ and $COMe_2$ in urine (cf. Fischer, A., 1934, 546) has been shown to be valueless by Bohrisch (Pharm. Zentr., 1907, **48**, 181 *et seq.*). The test proposed by the author (A., 1935, 513) produces the complex $Na_2[Fe^{\cdot\cdot}(CN)_4(CH_2Ac\cdot CO\cdot NH_2)_2],2H_2O$, or, with NH_2Me instead of NH_3, $Na_2[Fe^{\cdot\cdot}(CN)_4(NHMe\cdot CMe{:}CH\cdot CO_2\cdot)NH_3Me],2H_2O$. F. R. G.

Determination and excretion of flavins in normal human urine. A. Emmerie (Nature, 1936, **138**, 164).—Flavins are determined colorimetrically in urine after addition of PbS, elution with H_2O–C_5H_5N–AcOH, and oxidation with $KMnO_4$ in AcOH solution. Normal male urine gives a daily output of $819—1250\times10^{-6}$ g., and the hourly excretion varies between 30×10^{-6} and 50×10^{-6} g. After consumption of cooked ox liver an increased excretion of flavins occurs. L. S. T.

Uro- and copro-porphyrin-I in acute porphyrinuria. H. Fischer and H. Libowitzky (Z. physiol. Chem., 1936, **241**, 220—222).—Uroporphyrin-I (I) and the ester of uroporphyrin-III have been isolated from the urine of acute porphyrinuria. Uroporphyrin ester has m.p. 311° (corr.). In chronic porphyrinuria, (I) is probably the chief porphyrin produced. The Cu reaction indicates that urobilin frequently occurs in urine and fæces. W. McC.

Determination of fat in fæces. P. Muller (Nederl. Tijds. Geneesk., 1935, **79**, 3960—3962; Chem. Zentr., 1935, ii, 2712).—Extraction with acid $COMe_2$ is followed by evaporation and extraction of the residue with light petroleum. H. N. R.

Acetonæmia in goats. A. T. Gilyard and R. T. Gilyard (Cornell Veter., 1935, **25**, 201—202).—The $COMe_2$ content of a goat in late twin pregnancy in a state of paresis was lowered by injection of glucose. Ch. Abs. (*p*)

Mineral exchange between plasma and erythrocytes in Addison's disease. F. Schmitt and W. Basse (Arch. exp. Path. Pharm., 1936, **181**, 581—583).—In a case [Cl′] was low in the plasma and [Cl′], [Na˙], and [Ca˙˙] low and [K˙] high in the erythrocytes. Administration of cortin, NaCl, and $NaHCO_3$ had favourable results and partly restored normal vals. for the ionic concns. W. McC.

Chemical changes in the blood in Addison's disease and their alteration in response to treatment. E. N. Allott (Lancet, 1936, **230**, 1406—1411).—Cases of Addison's disease show low Na and Cl in the serum with high K and urea. Cortical extract appears to reduce K and urea to normal with little effect on Na and Cl. L. S. T.

Rôle of sodium in adrenal insufficiency. R. F. Loeb, D. W. Atchley, and J. Stahl (J. Amer. Med. Assoc., 1935, **104**, 2149—2154).—The decreased blood-Na observed in adrenal insufficiency results from increased excretion. Salt therapy mitigates symptoms of Addison's disease until destruction of adrenals is complete. Ch. Abs. (*p*)

Release of a histamine-like substance from lungs of guinea-pigs during anaphylactic shock. I. de B. Daly, S. Peat, and H. Schild (Quart. J. Exp. Physiol., 1935, **25**, 33—59).—The reported increase in intestine-contracting substance in lungs of sensitised guinea-pigs and decrease after anaphylactic shock (Watanabe, 1932) is not confirmed. A histamine-like substance appears in theperfusate of isolated lungs during shock. Ch. Abs. (*p*)

Soil, iron, and copper and iron in the prevention and treatment of anæmia in suckling pigs. H. C. H. Kernkamp (J. Amer. Vet. Med. Assoc., 1935, **40**, 37—58).—Development of anæmia was prevented by ingestion of powdered loamy soil in appropriate amounts. Use of Fe instead of soil was not effective, and addition of Cu to Fe had no additional beneficial effect. Ch. Abs. (*p*)

Determination of the biologically potent element (cobalt) in limonite. E. J. Underwood and J. F. Filmer (Austral. Vet. J., 1935, **11**, 84—92).—The active element is Co, deficiency of which in foods causes enzoötic marasmus. Ch. Abs. (*p*)

Castle's intrinsic factor in pernicious anæmia. C. C. Ungley and R. Moffett (Lancet, 1936, **230**, 1232—1235). L. S. T.

Spontaneous appearance of beri-beri symptoms in the mandarin duck (*Aix galericulata*, L.) kept in captivity. K. Li-Pin (Compt. rend. Soc. Biol., 1935, **119**, 1114—1115). R. N. C.

Renal changes in biliary stasis and decompression in cats. H. L. Stewart, A. Cantarow, and D. R. Morgan (Arch. Path., 1935, **19**, 807—818).—Changes in the distribution of stainable lipins are examined. Ch. Abs. (*p*)

Nitrogen and sulphur metabolism in Bright's disease. G. B. Grabfield and B. Prescott (Arch. Int. Med., 1936, **57**, 1081—1084).—The N : S ratio of urinary protein in nephrosis is 30 : 1, in glomerular nephritis and other syndromes 20 : 1, and normally 250 : 1. E. D. Y.

Histological changes in the enamel and dentine of the rat incisor in acute and chronic experimental fluorosis. I. Schour and M. C. Smith (Arizona Agric. Exp. Sta. Tech. Bull., 1934, No. 52, 69—91).—F probably exerts a direct local action on the enamel-forming cells. Changes observed in enamel and dentine are not produced primarily by changes in blood-Ca and -P or by disturbances of the parathyroid. A. G. P.

Distribution of ions between plasma and erythrocytes. (A) In normal and hypochloræmic diabetics. (B) In nephritis. (C) In intestinal diseases. F. Schmitt (Arch. exp. Path. Pharm., 1936, **181**, 563—569, 570—574, 575—580).—(A) Sharp separation of erythrocytes from plasma is attained by using a special type of centrifuge tube. In the erythrocytes of hypochloræmic diabetics $[Cl']$ is very high and $[Na^{\cdot}]$ (frequently), H_2O, and cations are low. In the plasma $[Na^{\cdot}]$ is low and $[K^{\cdot}]$ and $[Ca^{\cdot\cdot}]$ are high.

(B) In the erythrocytes of nephritis (hypochloræmic) $[Cl']$ is high and $[Na^{\cdot}]$ normal. In the plasma $[Na^{\cdot}]$ is low. When hyperchloræmia occurs $[Na^{\cdot}]$ is normal in the plasma but $[Cl']$ and (frequently) $[Na^{\cdot}]$ are high in the erythrocytes. In eclamptic uræmia the concn. of all electrolytes in the erythrocytes is high and plasma-Na is normal. Acidosis occurs in all cases.

(C) In stenosis of the pylorus there is genuine hypochloræmia. In carcinoma of the stomach and in cases of operable tumours there are no changes in the distribution of the ions. In cases of inoperable tumours $[Cl']$ in the erythrocytes is low (lower limit 92 mg. per 100 c.c.). W. McC.

Citric acid in blood and urine. O. Oestberg (Z. ges. exp. Med., 1934, **94**, 442—452; Chem. Zentr., 1935, ii, 3256).—Citric acid (I) is > normal in the blood in decompensation of the heart and diabetes mellitus, and less in inflammatory diseases, particularly pleurisy; the changes are associated with metabolic disturbances. (I) excretion can be altered by administration of acid or alkali without affecting blood-(I), with which it is unrelated. R. N. C.

Sodium chloride in diphtheria. A. Maclean (Lancet, 1936, **231**, 129—131).—Administration of NaCl has a beneficial effect. There is probably a deficiency of Na and Cl in the blood-serum in the acute stage of diphtheria. L. S. T.

Muscular dystrophies. Presence of simple guanidine derivatives in the urine. M. X. Sullivan, W. C. Hess, and F. Irreverre (J. Biol. Chem., 1936, **114**, 633—637).—From the urine of 70% of the cases of muscular dystrophy studied, guanidine (I) was isolated after treatment with $AgNO_3$ and $Ba(OH)_2$. Aq. solutions of gluco-cyamine and -cyamidine, but not of creatine, creatinine, or arginine, yield (I) by this treatment. Normal individuals do not excrete (I). H. D.

Prevention of nutritional encephalomalacia in chicks by vegetable oils and their fractions. M. Goettsch and A. M. Pappenheimer [with A. Hart] (J. Biol. Chem., 1936, **114**, 673—687).—The protective factor against nutritional encephalomalacia of chicks in certain edible oils is EtOH-sol., stable to heat, ultra-violet irradiation, and aëration, and is present in the unsaponifiable fraction. H. D.

Lipin exchange in the post-encephalitic syndrome. L. Bargi (Minerva med., 1935, II, 71–78).—An average increase of 42% in neutral fats, 30% in free cholesterol, and 14% in phosphatides in blood is recorded. Ch. Abs. (*p*)

Influence of p_H and of the alkaline reserve on the production and regression of experimental exophthalmia. J. Lévy, L. Justin-Besançon, and D. Kohler (Compt. rend. Soc. Biol., 1936, **122**, 1058—1060).—Exophthalmia in ephedrinised dogs is diminished by acidosis and its regression augmented, whereas alkalosis has a contrary effect. H. G. R.

Gout. Changes in symptoms and purine metabolism produced by high-fat diets in four gouty patients. L. M. Lockie and R. S. Hubbard (J. Amer. Med. Assoc., 1935, **104**, 2072—2075).—High-fat diet increased blood-uric acid, the effect persisting after changing to a high-carbohydrate, low-fat diet. Ch. Abs. (*p*)

Paroxysmal hæmoglobinurias. L. J. Witts (Lancet, 1936, **231**, 115—120).—A lecture. L. S. T.

Hyperglycæmia in fasted rabbits following injury in the pituitary region. D. J. Dawson and A. Milne (Quart. J. Exp. Physiol., 1935, **25**, 69—76). Ch. Abs. (*p*)

Iodine metabolism in goitre. L. Scheffer and L. von Megay (Klin. Woch., 1935, **14**, 1360—1362).—I is retained, excretion falling to about half the normal val. Blood-I oscillates considerably. R. N. C.

Metabolism of inorganic salts and water in hepatic disturbances. I, II. H. Shigemi (Japan. J. Gastroenterol., 1935, **7**, 12—18, 19—22).—I. In various hepatic infections, blood-K and -Ca tended to decrease, -Na to increase, and -Mg to remain unchanged. Hepatic injury in rabbits induced by $CHCl_3$, CCl_4, P, hepatotoxin, or ligation of the bile duct produced variable results.

II. Following liver injury by CCl_4 or ligation of the bile duct, the Ca, Mg, K, and Na contents of the heart, liver, spleen, and kidney of rabbits tended to decrease, the change being most marked in the liver. Ch. Abs. (*p*)

Spontaneous ketonuria from a ketogenic diet in hepatic patients. L. Cannavo and I. Capizzi (Diagnostica tec. lab. [Napoli], 1935, 6, 197—211).—Changes in ketonuria after feeding stearic acid are used in the diagnosis of parenchymal hepatic deficiency. β-Hydroxybutyric acid is the principal urinary product. The resulting increase in total org. acids in urine is not ∝ the increase in "keto-acids." Ch. Abs. (*p*)

Evidence for placental origin of the excessive prolan of late pregnancy toxæmia and eclampsia. G. V. S. Smith and O. W. Smith (Surg. Gynecol. Obstet., 1935, **61**, 175—183).—Sera of toxæmic and eclamptic patients have the same action on hypophysectomised rats as do sera of normal women. Placentas from such patients contain excessive prolan (I) and low levels of œstrin. Excessive (I) originates in the placenta and probably causes toxæmia and eclampsia. Ch. Abs. (*p*)

Physiology of pregnancy in rats. Mechanism of parturition. Effect on female rats of antenatal administration of œstrin to the mother. A. M. Hain (Quart. J. Exp. Physiol., 1935, **25**, 131—143).—Injection of œstrin (I) frequently prolonged the gestation period and modified the corpus urethræ of surviving female fœtuses. Synergism between (I) and oxytocin observed in mice does not exist in rats. Administration to pregnant rats of placenta, pituitary, uterus, and blood of parturient rats did not cause abortion. Ch. Abs. (*p*)

Protection of mice against streptococcal and other infections by *p*-aminobenzenesulphonamide and related substances. G. A. H. Buttle, W. H. Gray, and D. Stephenson (Lancet, 1936, **230**, 1286—1290).—*p*-$NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ (I) protects mice against infection by streptococci of different serological types, but not by staphylococci or pneumococci. There is some protection against meningococcal infection. Streptococcicidal action disappears when the no. of $SO_2 \cdot NH_2$ groups attached to the C_6 is increased to 3. *p*-$NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NHPh$ is as active as (I), but the acid itself has a smaller protective action. Azo-compounds derived from (I) and phenolic cinchona alkaloids are inferior to prontosil. L. S. T.

Chemical nature of tetany. D. E. Babcock (J. Chem. Educ., 1936, **13**, 317—319).—A discussion. L. S. T.

Pathophysiology of fat metabolism in thyroid diseases. S. Leites, E. Sorkin, and A. Agaletzkaja (Z. klin. Med., 1935, **128**, 407—416; Chem. Zentr., 1935, ii, 2836—2837).—Blood-fat is not affected in hyperthyroidism by feeding with butter, but is increased in hypothyroidism, being restored to normal by thyroxine or thyroidin. Blood-ketones are increased in both cases. R. N. C.

Action of 3 : 5-di-iodotyrosine in the treatment of hyperthyroidism. E. Delcourt-Bernard (Rev. Belge Sci. méd., 1934, **6**, 1—28; Chem. Zentr., 1935, ii, 3255).—The action is similar to that of Lugol's solution. R. N. C.

Selective absorption of ascorbic acid by tumour tissue from the guinea-pig. E. Boyland (Biochem. J., 1936, **30**, 1221—1224).—The indophenol-reducing material [probably mainly ascorbic acid (I)] of guinea-pig sarcoma (Dael and Biltris) is greatly reduced in amount when the animal is kept on a scorbutic diet; injected (I) is then selectively absorbed by the tumour and by those tissues which normally contain (I). The (I) content of the tumour is about the same as that of liver. W. McC.

Relation between tumour-lipins and length of life of persons suffering from tumours. R. Bierich and A. Lang (Fette u. Seifen, 1936, **43**, 105—106).—The higher is the cholesterol content of a tumour the shorter is the expectation of life of the patient after removal of the tumour by operation. Active cancer cells may contain 0·9—5% of cholesterol. F. C. B. M.

Indophenol-reducing substance in Jensen rat sarcoma. A. E. Kellie and S. S. Zilva (Biochem. J., 1936, **30**, 1216—1220).—Spectrographic and biological examination of sarcoma extracts indicate that almost all the indophenol-reducing material which it contains is *l*-ascorbic acid. W. McC.

Factors from normal tissues influencing the growth of transplanted cancer. D. A. MacFadyen and E. Sturm (Science, 1936, **84**, 67—68).—A tumour-inhibiting action of the H_2O extract of the Et_2O-insol. fraction of the rabbit, mouse, and cow mammary gland, and a tumour-stimulating property of the Et_2O-sol. fraction of the same tissues, have been established. There appears to be a partial neutralisation of the two forces in the aq. extract of the unfractionated mammary tissue. Further support is thus given to the view that active normal tissues contain two factors, one inhibiting and the other augmenting the multiplication of cells. L. S. T.

Thioglycerol: a more stable thiol compound for use in healing wounds. L. E. Sutton (J. Amer. Med. Assoc., 1935, **104**, 2168—2171).—Rapid healing follows use of $C_3H_5(OH)_2 \cdot SH$ in glycerol or tragacanth (1 in 5000). Ch. Abs. (*p*)

Silver manganite (simanite) in wound treatment. A. Schweitzer (Med. Klinik, 1935, **31**, 1175—1176; Chem. Zentr., 1935, ii, 2974). R. N. C.

Growth in relation to nutrition. H. von Hoesslin (Z. Biol., 1936, **97**, 229—243).—Four male dogs of the same litter were given diets in which (*a*) carbohydrate, (*b*) protein, (*c*) fat and starch, and (*d*) fat alone predominated. The first grew less quickly than the second but ultimately attained an equal size. The third, which received a diet containing only 10·45% of protein, still attained a size equal to that of the others although hair-growth was deficient. The rate of growth depended on the relative availability of the calorific val. of the diet. P. G. M.

Influence of intermittent supply on growth of albino rats. R. Sasaki and N. Ando (J. Agric.

Chem. Soc. Japan, 1935, **11**, 316—320).—Rats receiving intermittent supplies of protein required a longer time to attain standard growth. The wt. of organs was unaffected. CH. ABS. (*p*)

Chimpanzee metabolism. F. G. BENEDICT and J. M. BRUHN (Proc. Nat. Acad. Sci., 1936, **22**, 394—397).—Data for fasting R.Q. and basal heat production are recorded. A. G. P.

Biochemistry of hibernation. D. FERDMAN and O. FAINSCHMIDT (Ukrain. Biochem. J., 1932, 5, 20—57).—During the hibernation of *Citellus gutatus*, the creatinephosphoric acid, adenosine pyrophosphate, hexose monophosphate, the total acid-sol. P, and the total P of the voluntary muscle decrease, but the inorg. P rises. Similar results are obtained for the heart-muscle and blood. The reducing substances of the blood decrease. W. O. K.

Changes in the physicochemical constants of hen-egg plasma on incubation. S. S. PEROV and K. DOLINOV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1932, No. 3, 3—20).—Data for κ and n are given. CH. ABS. (*p*)

Effect of *Treponema pallidum* infection on metabolism of rabbit testis. R. M. KRAFT, C. S. ROBINSON, and S. HARRIS (Amer. J. Syphilis Neurol., 1935, **19**, 354—363).—The rate of metabolism was decreased without change in type. CH. ABS. (*p*)

Humidity and insect metabolism. K. MELLANBY (Nature, 1936, **138**, 124—125).—The rate of metabolism and respiration of many insects are controlled by temp. and unaffected by changes in humidity. L. S. T.

Destruction of oak by the death-watch beetle. A. G. NORMAN (Biochem. J., 1936, **30**, 1135—1137).—Analyses of the frass in oak timber attacked by the larvæ of the beetle (*Xestobium rufovillosum*) indicate that the carbohydrate and especially the cellulose is predominantly utilised as food (cf. A., 1930, 262). W. O. K.

Metabolism of cartilage. E. G. L. BYWATERS (Nature, 1936, **138**, 30—31).—The metabolism of cartilage is anaërobic. Lactic acid is formed from glucose at a rate of approx. 0·2 cu. mm. of CO_2 (from H carbonate solution) per mg. dry wt. per hr. In presence of methylene-blue an immediate, large increase in O_2 uptake occurs. L. S. T.

Metabolism of cartilage. F. DICKENS and H. WEIL-MALHERBE (Nature, 1936, **138**, 125—126; cf. preceding abstract).—As with medulla of kidney (this vol., 629), the same association of anaërobic type of metabolism and poor O_2 supply has been found for the rib cartilage of the rat. For medulla of kidney, cartilage, and tumours the ratios of respiration, aërobic and anaërobic glycolysis are similarly related. L. S. T.

Protein, fat, and carbohydrate metabolism in the white rat. II. Effect of fasting. R. WETZEL, H. WOLLSCHITT, H. RUSKA, and T. OESTREICHER (Arch. exp. Path. Pharm., 1936, **181**, 703—738; cf. A., 1935, 1152).—The effect of fasting for various periods on the fat, protein, and carbohydrate contents of the organs of adult males and on the wt. of the organs, the I val. of the fats, and the tissue respiration has been determined. W. McC.

Effect of feeding (A) white mice, (B) young foxes, with the proto-acid of peas. I. LEONTEV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1931, No. 1, 93—94; 1935, No. 7, 95—100).—(A) White mice thrive equally well when the proto-acid (I) is substituted for casein in the diet.

(B) Young foxes thrive on a diet in which (I) is the sole protein constituent. CH. ABS. (*p*)

Effect of parenteral injection of amino-acids and related substances on creatine formation and storage in the rat. H. H. BEARD and T. S. BOGGESS (J. Biol. Chem., 1936, **114**, 771—782).—100 mg. of creatine (I), glycocyamine, arginine (II), histidine (III), glycine (IV), alanine, serine, and valine for 1 day gave 6—32% increases in muscle-(I). At the end of 2 days the increase for the first four varied from 16 to 40%, but that due to (IV) had disappeared. 200-mg. doses of (II) and (III) for 1 or 2 days gave an increase of 30—40% in muscle (I), whilst 200 mg. of (IV) caused <10% increase. Injection of 100 mg. of (II) with 100 mg. of (IV) for 2 days gave a 41% increase, which was due to (II) alone. 200 mg. of (II) for 1 day caused a 43% and 22% increase, respectively, in stomach- and liver-(I), whilst 100 mg. of (III) increased stomach-(I) by 19%. Formation of (I) from its precursors occurs chiefly in the muscles and its origin and storage are discussed. J. N. A.

Compounds of serum-proteins with polysaccharides. J. JANICKI and K. KASPRZYK (Biochem. J., 1936, **30**, 1526—1531).—H_3PO_4-free amylose combines with proteins. Euglobulin is the only serum-globulin which combines with non-ionised polysaccharides; pseudoglobulin has practically no binding power, whilst albumins combine to only a small extent. Albumin coagulated by boiling or by change of p_H does not bind amylose. Fats do not affect combination between serum-euglobulins and amylose. J. N. A.

Biological behaviour of clover- and potato-proteins in metabolism. A. BICKEL, R. SANDER, and J. SCHILLING (Münch. med. Woch., 1935, **82**, 1482—1485; Chem. Zentr., 1935, ii, 2693).—Data for changes in the N balance, based on tests with rats, are discussed. The biological behaviour of these proteins is different from that of animal proteins. H. J. E.

Loss of protein from working heart muscle. K. LISSÁK and J. HOYOS (Arch. exp. Path. Pharm., 1936, **181**, 607—609; cf. *ibid.*, 233).—Ringer's solution takes up from beating hearts protein (I) which, in low concn. (1 : 10^3—10^5), inhibits the action of Na oleate on the frog's heart. The amount of (I) given up to the solution is increased by electrical stimulation of the vagosympathic nerve. W. McC.

Rôle of carnosine in muscle activity. Influence of training on the content of the muscle in chromogenic substance. P. NORMARK and E. SAVRON (Ukrain. Biochem. J., 1932, 5, 17—19).—The chromogenic material in the biceps femoris of the rabbit determined in protein-free extracts by the method of Hanke and Koessler is increased after training by electrical stimulation. W. O. K.

Renal function tests. Modern methods of investigation. III. Phenolsulphonephthalein and other dyes. M. Fiorentino, E. Macchia, and N. Sanguigno (Diagnostic tec. lab. [Napoli], 1935, **6**, 89—115).—A review. Of various dyes considered, phenolsulphonephthalein is best. Ch. Abs. (*p*)

Uric acid-excreting function of the liver in renal disturbances. I—III. S. Matsumoto (Japan. J. Gastroenterol., 1935, **7**, 1—6, 7—8, 9—11).—I. Injection of uric acid (I) into the bloodstream of rabbits after extirpation of one or both kidneys or ligation of renal vessels or ureters caused an increased output of (I) in bile, as compared with injection into normal rabbits.

II. In kidney disturbance caused by injection of U nitrate, cantharidin, or *Trimeresurus riukiuanus*, elimination of (I) in bile is increased.

III. Extirpation of the kidneys accelerates the (I)-excreting function of the liver. Ch. Abs. (*p*)

Disturbance and regulation of cholesterol metabolism. I. Effect of liver extract on the disturbed cholesterol metabolism. II. Thyroid and cholesterol metabolism. A. O. Schally (Z. klin. Med., 1935, **128**, 365—375, 376—385; Chem. Zentr., 1935, ii, 2690).—I. Liver extracts restore increased or diminished serum-cholesterol (I) to normal.

II. (I) is reduced in hyperthyroidism, the fall $\propto$ the extent of the disease; it is increased by therapy, particularly strumectomy. (I) is also depressed in other diseases of the thyroid, which has an inhibiting effect on (I) metabolism. R. N. C.

Chemistry of fatigue. A. Palladin, L. Palladina, and E. Persova (Ukrain. Biochem. J., 1932, **5**, 7—16).—The lactic acid content of the biceps femoris of rabbits is increased after electrical stimulation for 5 min., but with trained muscle a decrease occurs. W. O. K.

Metabolism of organic salts. G. Suranyi (Nourisson, 1934, Nov., 7 pp. [Sep.]).—The rôle of glutathione and cysteine in intermediate metabolism is examined. Ch. Abs. (*p*)

Metabolism of sulphur. Determination of cystine in normal urine. G. Medes (Biochem. J., 1936, **30**, 1293—1297).—The method for the determination of cystine (I) (this vol., 881) is applied to urine and compared with other methods. Glutathione, ergothioneine, and uric acid do not interfere. About 70% of the total S·S in urine consists of (I). H. D.

Recent researches on fat metabolism. P. E. Verkade (Bull. Soc. Chim. biol., 1936, **18**, 989—1013).—A lecture.

Distribution of fats introduced into the organism. G. Peretti, L. Reale, and L. Cioglia (Arch. Ital. Biol., **90**, 59—70; Chem. Zentr., 1935, ii, 2693).—Fats administered intravenously or orally cause a rise in the fatty acid (I) content of the blood, followed by a const. period and a fall. The (I) in the liver increases steadily (44 hr.) and then falls. H. J. E.

Glycogen and carbohydrate content of the fatty tissue of rats given unbalanced diets after fasting. R. Wetzel and T. Heid (Arch. exp. Path. Pharm., 1936, **181**, 689—702).—The effects of feeding unbalanced (all carbohydrate, protein-rich, fat-rich) diets on the contents of glycogen and reducing substances in the fatty tissues of rats after fasting have been examined. W. McC.

Correlation between rates of intestinal absorption of some simple sugars. H. G. K. Westenbrink and A. Middelbeek (Arch. Néerland. Physiol., 1936, **21**, 283—293).—The rate and course of intestinal absorption of galactose (I) in rats approximates to that of glucose (II) but not to that of xylose; for each sugar variations occur with different rats. The absorptions of dietary constituents are generally independent of each other but with substances such as (I), (II), and fructose some degree of interrelationship is evident. F. O. H.

Relative velocities of the absorption of different sugars from the intestine of rat and pigeon. H. G. K. Westenbrink (Nature, 1936, **138**, 203—204).—The ratios of the absorption velocities of *d*-galactose, *d*-glucose, *d*-fructose, *d*-mannose, *l*-xylose, and *l*-arabinose are fundamentally the same for rats and pigeons fed on the same diet. L. S. T.

Carbohydrate metabolism of the mammary gland *in vitro*. C. Antoniani and A. S. Clerici (Atti R. Accad. Lincei, 1936, [vi], **23**, 73—76; cf. A., 1932, 1059; 1933, 83).—Finely-divided mammary gland (lactating cow) transforms phosphoglyceric acid into AcCO$_2$H with liberation of inorg. P (cf. A., 1934, 1261). Non-lactating (virginal) gland merely hydrolyses the ester. E. W. W.

Lactacidogen and lactic acid in the surviving pigeon brain. H. Gorodisski and S. Epelbaum (Ukrain. Biochem. J., 1932, **5**, 87—100).—During 2 hr. in isotonic NaCl solution, the lactacidogen (I) content of surviving pigeon brain decreases. The addition of starch or glucose is without effect. Lack of O$_2$ accelerates and electrical stimulation retards the disappearance of (I). W. O. K.

Carbohydrate catabolism in cerebral cortex. K. C. Dixon (Biochem. J., 1936, **30**, 1479—1482).—The rates of anaërobic and aërobic carbohydrate catabolism have been calc. from the rates of respiration and glycolysis. The former is the greater, and the Pasteur effect is in operation in slices of cerebral cortex acting on glucose *in vitro*. Addition of KCl raises the aërobic val. to the anaërobic. H. G. R.

Effect of rise in temperature on the carbohydrate catabolism of cerebral cortex. K. C. Dixon (Biochem. J., 1936, **30**, 1483—1488).—The rates of respiration and of aërobic glycolysis at 42° are slightly $>$ those at 37°, but are considerably increased at 45°. An abrupt rise in anaërobic glycolysis is observed above 42° but there is a rapid fall at 45°. The Meyerhof quotient being normal, there is no sp. inhibition in the Pasteur effect with temp., and the rates of carbohydrate catabolism at various temp. do not follow Arrhenius' law. H. G. R.

Ossification by means of tissue culture. R. Sasaki (Z. Klin. Path. Hämatol. [Japan], 1933, 2, 1246).—In tissue cultures of the surfaces of frontal bones of chick embryos, oxidase (I) and Fe appeared simultaneously in the tissue, followed by Ca deposition in 1—2 days. A close relationship between (I), Fe, and Ca is established. Ch. Abs. (*p*)

Cortico-adrenal insufficiency and potassium metabolism. I. Determination of potassium in small amounts of blood and tissues. II. Blood-potassium of normal and adrenalectomised cats. III. Potassium content of skeletal and cardiac muscle in cortico-adrenal insufficiency. R. Truszkowski and R. L. Zwemer (Biochem. J., 1936, 30, 1345—1353).—Methods for determination of K in 0·2 ml. of blood and in small amounts of muscle are described. Normal vals. (19 cats) were: plasma 19·3, serum 20·2, and whole blood 21·4 mg. of K per 100 ml. The vals. for blood-K in 18 bilaterally adrenalectomised cats varied within wide limits (11 to 46 mg. per 100 ml.) for different animals at different times after the operation. The most consistent effect was a rapid rise in blood-K to a max. val. on the 3rd or 4th day. An average of 0·415% wet wt. or 1·9% dry wt. was found for skeletal muscle of animals in the terminal stage of adrenal insufficiency and of 275 and 1277 mg. per 100 g., respectively, for myocardium. The vals. for wet wt. are $<$ and for dry wt. $>$ for normal cats. The syndrome of cortico-adrenal insufficiency is intimately associated with a disturbance of K metabolism. P. W. C.

Rôle of non-electrolytes in imbibition. D. Kohler (Compt. rend. Soc. Biol., 1936, 122, 1050—1052).—Imbibition of desiccated *Laminaria flexicaulis* is decreased by non-electrolytes in the early stages, but later is increased. H. G. R.

Influence of reaction of the external medium on the survival and the p_H of the hæmolymph of oysters. A. Jullien and J. G. Richard (Compt. rend. Soc. Biol., 1936, 122, 1106—1108).—The optimum p_H for the Portuguese oyster is 7·5, but it will survive for some time at a p_H between 4·5 and 9·2. The p_H of the internal medium (6·1—8·3) is 0·3—0·4 $<$ that of the external medium. H. G. R.

(A) Relation between natural tolerance to heroin and the partition coefficient of the drug for the central nervous system. (B) Changes in partition coefficient in heroin habituation. (C) Changes in partition coefficient of morphine by heroin habituation. (D) Changes in partition coefficient of heroin by morphine habituation. (E) Change in partition coefficient of morphine by cocaine habituation. M. Watanabe (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 32—34, 34—35, 36, 36—37, 37—38). Ch. Abs. (*p*)

Action of nymphalin on the heart and blood-vessels. M. Ryszkowska (Wiad. farm., 1935, 62, 249—251, 263—266; Chem. Zentr., 1935, ii, 2695).—Nymphalin, a glucoside from *Nymphea alba* and *Nuphar luteum*, has cardiac activity but does not cause constriction of the blood-vessels in therapeutic doses. H. N. R.

Contradictory actions of caffeine, coramine, and metrazole. A. H. Maloney (Quart. J. Exp. Physiol., 1935, 25, 155—166).—The depressant action of barbital was accentuated by caffeine, coramine (I), or metrazole (II) under certain conditions. Transitory reverse effects occurred with certain dosages of (II) and (I). Ch. Abs. (*p*)

(A) Resting metabolism of the frog ventricle. (B) Influence of depressants on rate of asphyxiation of frog ventricle. A. J. Clark (Quart. J. Exp. Physiol., 1935, 25, 167—180).—(A) Examination of ventricles poisoned with $CH_2I\cdot CO_2H$ indicates that phosphagen is utilised by the resting as well as by the contracting ventricle.

(B) Data for resting and contracting ventricles at different temp. are given. Acetylcholine reduces the metabolism of arrested ventricles by 50%. Ch. Abs. (*p*)

Observations on perfused lungs of guinea-pigs. A. S. Dale and B. Narrayana (Quart. J. Exp. Physiol., 1935, 25, 85—97).—Effects of acetylcholine (I), atropine (II), and eserine (III) on broncho- and vaso-constriction are examined. The action of (I) was counteracted by (II) but not by (III). Ch. Abs. (*p*)

Barbiturates. XV. Excretion of barbital in normal and nephritic subjects. W. P. Argy, C. R. Linegar, and J. M. Dille (J. Pharm. Exp. Ther., 1936, 57, 258—263).—In men, kidney disease (arteriosclerosis or nephritis) causes a marked reduction in the urinary output of barbital administered orally. A. L.

Diuretic action of the digitalis group. I. Matsuyama (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 166—167).—Effects of digalen, diagfolin, pangital, digitoxin, scillaren, and strophanthin are compared in different animals. Ch. Abs. (*p*)

Mechanism of uric acid excretion of cinchophen. H. Oka (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 170—171).—Cinchophen lowers the excretion threshold in the kidney, thereby decreasing the uric acid concn. in blood. Ch. Abs. (*p*)

Influence of *o*-, *m*-, and *p*-hydroxybenzoic acid on the gaseous metabolism of the kidney in relation to urine formation. K. Tamura and G. Kihara (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 171—175).—The *m*-acid is more, and the *p*-acid less, irritant than salicylic acid. The theobromine Na salts of *p*- and *m*-acids are not less diuretic but more irritant than the corresponding *o*-acid salt. Ch. Abs. (*p*)

Phenylurethane anæsthetics. II.—See this vol., 1103.

Intensity of action of anæsthetics as a function of their emulsified state or solution in the blood. N. Lazarev (Compt. rend. Soc. Biol., 1936, 122, 891—893).—With increasing partition coeff. (oil–

H_2O), the hæmoglobin-fixation and anæsthetic activity increase. H. G. R.

Local anæsthetic actions of certain pyrazoline and quinoline compounds. H. K. Sinha (J. Pharm. Exp. Ther., 1936, **57**, 199—220).—Using 1-phenyl-5-(4′-methoxy-3′-ethoxyphenyl)-3-(β-*N*-piperidinoethyl)pyrazoline hydrochloride (I), di-(quinolyl-8′-methyl)-1 : 4-piperazine tetrahydrobromide (II), and 8-(diethylaminoethylethylaminomethyl)quinoline trihydrobromide (III), a comparison of the three methods of determining anæsthetic acitivity, viz., (*a*) the rate of paralysis of the frog's sciatic nerve, (*b*) the rabbit's cornea, and (*c*) the human wheal methods, indicates that the simplest method is to determine the concn. of the drug which produces anæsthesia for a standard time and this method is applied to methods (*b*) and (*c*). With method (*a*) results are variable. (I) and (II) may be of val. for clinical application to mucosæ and for infiltration anæsthesia, whilst (III) is equal to novocaine for nerve-trunk anæsthesia. A. L.

Sensitivity of various animals towards anæsthetics. A. Brussilovska (Compt. rend. Soc. Biol., 1936, **122**, 983—895).—The concns. in the blood of various anæsthetics lethal to frogs and mice are given. H. G. R.

Galvano-narcosis as a means of investigating the action of hypnotics and narcotics on the frog. P. Adler and C. Hradecky (Arch. exp. Path. Pharm., 1936, **181**, 541—552).—The min. current required to produce narcosis is reduced following administration of hypnotics and narcotics but is restored to the initial val. as the effect of these passes off, the strength of current required being (within limits) inversely $\propto$ the depth of narcosis produced by the substances. 17—36% reduction of the min. effective dose corresponds with 50% reduction in the current strength. W. McC.

Chemical transmission of the nervous influx at the level of the central synapses. G. Benetato and N. Munteanu (Compt. rend. Soc. Biol., 1936, **122**, 1128—1132).—A substance similar to acetylcholine is formed in the venous blood of the bulb during stimulation of the vagus. H. G. R.

Rôle of acetylcholine in transmission of nervous stimulation in striated muscle. L. Lapicque (Compt. rend. Soc. Biol., 1936, **122**, 990—993).—It is suggested that acetylcholine is formed not between the nerve and the muscle but in the muscle itself and serves to generalise the stimulations. H. G. R.

Gel formation in hen egg plasma. K. Dolinov (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1931, No. 2, 21—27).—Na salicylate (5—35% solution) gelatinises white plasma and in concns. >4·9% gelatinises yolk plasma. Ch. Abs. (*p*)

Action of ethylene on cell processes. F. F. Nord (Austral. J. Exp. Biol., 1936, **14**, 131—133).—Polemical (cf. A., 1935, 1165). H. G. R.

Effect of pyocyanine on the animalisation of the sea-urchin caused by calcium-free sea-water and sodium thiocyanate. J. Runnström and D. Thörnblom (Naturwiss., 1936, **24**, 447).—Eggs of the sea-urchin were treated with a mixture of 90 parts of Ca-free sea-H_2O and 10 parts of 0·54*M*-NaCNS, and with this mixture together with $2·15 \times 10^{-4}$% of pyocyanine (I). They were then fertilised and hatched. After 12 hr. treatment with the solution containing (I), 80% of the eggs were animalised, whereas in a solution without (I) only 10% were animalised. The curves expressing animalisation against time of treatment are S-shaped and agree with the formula of Rahn (this vol., 506). (I) accelerates the respiration of the unfertilised egg. A. J. M.

Food allergy. H. Stevens (Oil and Soap, 1936, **13**, 162—165).—Clinical evidence concerning the allergic effects attributed to ingested cottonseed products is often incomplete, and the conclusions are therefore invalidated. E. L.

Effect of the epithelial cell and colloid substance on the thyroid gland, and of alcoholic hydrochloric acid extracts of the thyroid and of residues from such extracts on tissue respiration. K. Mune (Folia Endocrinol. Japon., 1933, **9**, 27—28).—The O_2 consumption of living extirpated tissues of rats was increased by treament with aq. extract of epithelial cell substance or EtOH–HCl extract of thyroid gland, but was decreased by aq. or EtOH–HCl extract of the colloid substance. Ch. Abs. (*p*)

Tyramine: its moderating effect on basal metabolism. P. Jacchia (Boll. Soc. ital. Biol. sperim., 1934, **9**, 276—279).—Tyramine administered orally to patients with normal basal metabolism causes a fall, a steady min. being reached in 3 hr. R. N. C.

Existence in blood and urine of substances promoting liver function. I. N. Mizuta and T. Matsuura (Japan. J. Gastroenterol., 1935, **7**, 23—35).—After extirpation of kidneys or in drug-induced nephritis rabbit's blood contains a substance promoting pigment excretion in the liver; it is sol. in H_2O and Et_2O, fairly stable in neutral and slightly acid media, but rapidly destroyed by alkalis. It also occurs in blood in cases of kidney malfunction. Ch. Abs. (*p*)

Influence of cations and carbohydrate on the formation of inorganic phosphoric acid during the autolysis of brain extracts. H. Gorodisski and S. Epschtein (Ukrain. Biochem. J., 1932, **5**, 101—112).—In autolysing extracts of pigeon's and cat's brains, "summarisches" H_3PO_4 (I) (inorg. H_3PO_4+creatinephosphoric acid) is formed, but at a constantly diminishing rate. $K^{\cdot}$, $Na^{\cdot}$, $NH_4^{\cdot}$, and $Ca^{\cdot\cdot}$ retard but $Mg^{\cdot\cdot}$ accelerates production of (I). Addition of glucose, galactose, glycogen, dextrin, and starch to the autolysing extract of cat's brain retards the reaction but maltose first retards and then accelerates it. W. O. K.

Influence of oral administration of saponin with adrenaline, ephedrine, and insulin on blood-sugar and -inorganic phosphorus contents. T. Ichijo (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharmacol. Soc., 1933, 54—56).—Saponin tended to increase the action of the three substances. Ch. Abs. (*p*)

3-Diethylaminomethyl- and 3-piperidomethylbenzdioxan do not enhance the hypoglycæmic

action of insulin in the dog. E. Zunz, J. Perla, and F. Jourdan (Arch. int. Pharmacodyn., 1935, 49, 470—474). R. N. C.

Site of action of barium, strychnine, and veratrine in the striated muscle of the toad. G. Russo (Arch. ital. Biol., 1934, **91**, 60—74; Chem. Zentr., 1935, ii, 3126). R. N. C.

Effect of adrenalone, ephedrine, and adrenaline on rabbit blood-sugar. K. Akimoto (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharmacol. Soc., 1933, 34—35).—Max. changes occur 30 min. after administration. Threshold doses for oral, rectal, and subcutaneous administration are compared. Ch. Abs. (*p*)

Biological identification of proteins. I, III—V, VII. I. Leontev. **VIII.** I Leontev and Z. Grafskaja, **IX, X, XII.** I. Leontev (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1931, No. 1, 61—65; No. 2, 69—71; 1932, No. 3, 51—55, 56—58; 1933, No. 3, 55—60; No. 4, 62—65, 60—61; No. 5, 61; 1935, No. 7, 65—66).—I. The proto-acid of peas produces no anaphylactic shock in rabbits.

III, IV. Injection of protein into cold-blooded animals produced no shock.

V. Neither " fibrinic acid " nor ovalbumin produced shock in guinea-pigs.

VII. Proteins of seed of watermelons, muskmelons, and pumpkins, tested biologically, were identical.

VIII. Proto-acid extracted from sunflower seed by NaOH produces no shock. That extracted by 10% aq. NaCl causes typical shock.

IX. Proto-acid from field nut, unlike the protein obtained by Osborne's method, causes no shock.

X. Proto-acid from yellow acacia (15% N) has the same immunological effect on guinea-pigs as does that of peas, beans, etc. and differs from the protein (Osborne's method) in producing no shock.

XII. The Me ester hydrochloride of glycinin (I) contained no lysine or tryptophan. Both (I) and the Me derivative produced shock. Guinea-pigs sensitised to (I) suffered shock when re-injected with methylglycinin and vice versa. Ch. Abs. (*p*)

Parenteral injection of proto-acid ("caseinic acid"). M. N. Tschukitscheva-Fedorova, V. A. Dalmatov, and I. P. Tschukitschev (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1931, No. 1, 68—74).—Effects of injected protein are due to the degree of dispersion of the protein and not to the fact that it is foreign to the organism. Rabbits tolerate large injections of proto-acid without pathological changes and retain the substance. Ch. Abs. (*p*)

Action of extremely minute amounts of protein ("caseinic acid") on blood pressure. I. P. Tschukitschev and B. Jordanski (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1932, No. 3, 21—22).—Increased blood pressure observed persists for a longer period than that produced by adrenaline. Ch. Abs. (*p*)

Artificial protein plasma. M. N. Tschukitscheva and I. P. Tschukitschev (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1933, No. 5, 35—38).—Injection of casein (I) into rabbits and dogs produced no ill-effects. (I) cannot be regarded as foreign to the organism (cf. Perov, this vol., 1038). Ch. Abs. (*p*)

Histochemical study of gold depôts in cells. R. Cohen (Compt. rend. Soc. Biol., 1936, **122**, 1123—1124). H. G. R.

Rôle of the reticulo-endothelial system in the chemotherapeutic action of arsenobenzene derivatives. I, II. M. Zolog and O. Comsia (Compt. rend. Soc. Biol., 1936, **122**, 1135—1137, 1138—1140). —I. Blockage or destruction of the reticulo-endothelial system increases the quantity of therapeutic agent available and the apparent activity is increased.

II. Blockage or destruction of the system prior to infection is without action on the course of the latter. Blockage before infection and 3 days before treatment has a favourable effect, whilst destruction slightly reduces the parasiticidal effect. H. G. R.

Action of arsenobenzene derivatives on experimental trypanosomiasis. M. Zolog and O. Comsia (Compt. rend. Soc. Biol., 1936, **122**, 1132—1134).—The active principle is dialysable and cannot be a toxalbumin. It is not necessary for the therapeutic substance to be reduced in the organism for it to acquire therapeutic properties. H. G. R.

Composition of food poor in heavy metals and its influence on rats. J. A. F. Kok [with C. Waal] (Arch. Néerland. Physiol., 1936, **21**, 247—265). —The prep. of a synthetic diet containing only traces of Cu and Fe is described. Rats on such a diet have a low hæmoglobin val., which is increased to normal levels by addition of Fe alone to the diet; growth is approx. normal but fatty degeneration of liver and kidney occurs. F. O. H.

High-potassium diet and the survival of adrenalectomised rats. R. A. Cleghorn and G. A. McVicar (Nature, 1936, **138**, 124).—These rats lived longer when the diet (Purina Dog Chow) containing cereals, meat, molasses, and vitamins was supplemented by bread. The low K content of the bread may have favoured survival. L. S. T.

Effect of weaning on the excretion of calcium in the urine of lactating rats. L. I. Pugsley (Biochem. J., 1936, **30**, 1271—1273).—The urinary Ca of lactating rats increases on weaning; the greatest effect is obtained by weaning 15 days after parturition. Removal of the mammary glands after 10 days' lactation causes no increased excretion of Ca over the pre-parturition rate. H. D.

Action of magnesium dithiosalicylate on the experimental elimination of cystine. J. Delphaut and S. Fleurent (Compt. rend. Soc. Biol., 1936, **122**, 957—958).—Excretion of cystine in the urine increases. H. G. R.

Action of intravenous and intramuscular injections of callicrein in man. E. K. Frey, E. Werle, and E. Sackers (Z. ges. exp. Med., 1935, **96**, 404—413; Chem. Zentr., 1935, ii, 3256). R. N. C.

Effect of intravenously-given callicrein on cerebrospinal fluid pressure. T. Reeke and E. Werle (Z. ges. exp. Med., 1935, **96**, 398—403; Chem. Zentr., 1935, ii, 3256). R. N. C.

Callicrein in the saliva and its intervention during the chemical transmission of the nervous influx. G. Ungar and J. L. Parrot (Compt. rend. Soc. Biol., 1936, **122**, 1052—1055).—Callicrein is the hypotensive substance in saliva and it may be the cause of vasodilation following stimulation of the lingual nerve. H. G. R.

Pharmacology of aromatic selenium compounds. S. Kondo (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 132—135).—Effects of OH-, $(OH)_2$-, and carboxy-derivatives of Ph_2Se and Ph_2Se_2 are recorded. Ch. Abs. (*p*)

Pharmacological action [of drugs] in hypervitaminosis-*B*. A. Allegri (Boll. Soc. ital. Biol. sperim., 1934, 9, 236—240). R. N. C.

Œstrogenic activity of certain phenanthrene and hydrophenanthrene derivatives. G. Pincus and N. T. Werthessen (Science, 1936, **84**, 45—46).—The activities in mice of the derivatives prepared by Fieser *et al* (this vol., 203) are recorded. The effect of constitution on activity is discussed. L. S. T.

Pharmacology of methylglyoxal. I. G. Araki (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 44—47).—Lethal dosages are determined. In alkalosis the val. was > that in acidosis. AcCHO rapidly disappears from blood, producing a marked decrease in alkali reserve. HCO_2H is among the decomp. products. Ch. Abs. (*p*)

Convulsants of the picrotoxin group. H. Kusumoto (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharmacol. Soc., 1933, 89—90).—Physiological data for coriamyrtin, tutin, picrotoxin, and picrotoxinine are given. Ch. Abs. (*p*)

Pharmacological action of tannic acid. VI. Minimum lethal dose by intravenous injection. U. Sammartino (Arch. Farm. sperim., 1936, **61**, 156—159).—The min. lethal dose in rabbits is 0·16 g. per kg. E. P.

Variations in blood-cholesterol and -sugar after slow, continuous, mesenteric injection of chlorinated arsenical water containing sodium hydrogen carbonate. E. Chabrol, J. Cottet, and J. Sallet (Compt. rend. Soc. Biol., 1936, **122**, 905—907).—A decrease in cholesterol and sugar occurs. H. G. R.

Pharmacology of sodium furfuracrylate. I. Effect on the frog heart. M. Noda (Aichi Igak. Zasshi, 1933, **40**, 1503).—The depressive effect of Na furfuracrylate (I) on the heart action was unaffected by previous administration of Gynergen, but was reinforced by adrenaline. The weakened contractions were not improved by $BaCl_2$. (I) affects the heart muscle directly. Ch. Abs. (*p*)

Anhidrotic action of agaric acid. K. Hattori (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 157—160).—Agaric acid acts on the parenchyma of sweat glands. Ch. Abs. (*p*)

Influence of phosphorus poisoning on the synthesis of mentholglycuronic acid. II. B. Nazarjanz (Ukrain. Biochem. J., 1932, **5**, 129—132; cf. A., 1935, 1533).—The impaired ability of rabbits poisoned with P and injected with menthol to synthesise mentholglycuronic acid is accompanied by pathological changes in the liver, involving fatty degeneration. Lesions of the kidney do not effect the synthesis of conjugated glycuronic acids. W. O. K.

Action of sulphur in experimental carbon monoxide poisoning. K. Voit and H. H. Schmidt (Münch. med. Woch., 1935, **82**, 1393—1395; Chem. Zentr., 1935, ii, 2842).—Injection of S prevents the erythrocytosis and hyperglycæmia arising from CO poisoning. H. N. R.

Bismuth poisoning. H. C. Lueth, D. C. Sutton, C. J. McMullen, and C. W. Muehlberger (Arch. Int. Med., 1936, **57**, 1115—1124).—A case report of a permanent blue discoloration of the skin as in argyria after prolonged treatment with Bi subnitrate (4 g. per day). E. D. Y.

Influence of chronic thallium poisoning on the function of the female sex organs of rats. T. Arashima (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 135—136).—In rats treated with $TlCl_2$ solutions, sex functions are affected only in association with nutritive changes. Ch. Abs. (*p*)

Effect of injection of potassium cyanide on hydrogen-ion concentration of blood plasma especially in relation to certain hormones. I. Effect of potassium on plasma-p_H. II. Relation to thyroid. III. Relation to insulin. N. Nakatsugawa (Folia Endocrinol. Japon., 1934, 9, 99—100).—I. Injection of 0·2—0·8 c.c. of 0·5% aq. KCN produced an initial increase in p_H, followed by a decline to < normal vals.

II. Fluctuations in p_H following injection are intensified by feeding small doses of thyroid gland. Large doses accelerated the second (declining) phase.

III. Injection of insulin, alone or with glucose, decreased the variations due to injection of KCN. Ch. Abs. (*p*)

Fluorides in Foochow waters and dental defects. T. H. Wang (J. Chinese Chem. Soc., 1936, 4, 172—177).—The occurrence of mottled dental enamel is related to the high F content of drinking H_2O. R. S.

Effect of age on sensitivity to metabolic poisons. H. Yamagata (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 142—150).—The O_2 intake of liver, kidney, and muscle tissues was decreased by As_2O_3 and increased by thyroxine to approx. the same extent in young and old rabbits in each case. Ch. Abs. (*p*)

Effect of age on sensitivity to blood poisons. T. Isobe (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 150—154).—Resistance of young rats to CO, HCN, H_2S, $NHPh{\cdot}NH_2$, and NH_2Ph was > that of adults. Splenectomy did not influence susceptibility. Ch. Abs. (*p*)

Mechanism of iodoacetate poisoning of muscle. A. Ghaffar (Quart. J. Exp. Physiol., 1935, **25**, 61—67).—The effect of $CH_2I{\cdot}CO_2Na$ (0·001*N*) on the glycolytic activity and lactic acid production of frog muscle is examined in relation to I liberation, time, and temp. CH. ABS. (*p*)

Toxicity of some cations to *Saprolegnia*. F. MOREAU and (MME.) F. MOREAU (Compt. rend., 1936, **202**, 2175—2177).—The inhibitory effect of the following cations (as 0·3—1·0% aq. chlorides) on the growth of *Achyla colorata* gives the series: Li > Na > K; Ba > Sr > Ca; Mg > Ca. F. N. W.

Pathological effects of poisons used for rodents. J. G. WRIGHT (Vet. Rec., 1936, **16**, 599—602).—A review of the pharmacological actions of HCN, As_2O_3, P, $BaCO_3$, red squill (I), and strychnine. Of these, $BaCO_3$ and (I) are the most suitable for poisoning rodents, but from a humane point of view a combination of one of these poisons with an appropriate narcotic is recommended. J. N. A.

Toxicity of flavins. R. KUHN and P. BOULANGER (Z. physiol. Chem., 1936, **241**, 233—238).—The following *iso*alloxazines are toxic to mice (rats on vitamin-B_2-free diet were also used) in the doses given (mg. per kg.): 9-Me- 125 (60 with rats and irradiated mice), 9-Ph- (I) 17, 9-CH_2Ph- 50, 9-*cyclo*hexyl- 50, 9-hydroxyethyl- 280, 9-dihydroxypropyl- 200, 6 : 8 : 9-Me_3-, 300—310, 9-OAc- 130: the following are less toxic: 6 : 9-Me_2- 350, 6 : 7 : 9-Me_3- 330, 9-acetyl-6 : 7-dimethyl- 775, and lactoflavin 340. Hence Me in the 6 : 7-positions reduces the toxicity. (I) loses its toxicity when heated with dil. aq. NaOH, being converted into a ketocarboxylic acid with loss of urea. The toxic doses of alloxazine and its 6 : 7-Me_2 derivative are 305 and 250, respectively. In some cases the toxicity is increased by irradiation of the animals. W. McC.

Pharmacological and toxicological properties of vinyl ether. H. MOLITOR (J. Pharm. Exp. Ther., 1936, **57**, 274—288).—For a 3-hr. anæsthesia, the toxicity of vinyl ether (I) to mice is 0·19 c.c. per litre of air. The corresponding vals. for Et_2O and $CHCl_3$ are 0·18 and 0·026 c.c., respectively. Decomp. of (I) is accompanied by loss in anæsthetic power, although there is no decomp. when it is circulated through the body. In low concn., Et_2O has a quicker action; (I), however, acts more rapidly at high concn., and recovery is always more rapid. A. L.

Value of sodium formaldehydesulphoxylate in mercury poisoning. W. E. ROBERTSON and V. L. TUCK (J. Chemother., 1935, **12**, 226—231). CH. ABS. (*p*)

Unsuccessful attempts to treat and prevent cyanide poisoning by dinitrophenol. R. HAZARD and P. HAUTEVILLE (J. Pharm. Chim., 1936, [viii], **24**, 5—8). H. D.

Biological action of metals irradiated by the quartz lamp. III. I. M. GOLDBERG and V. G. BOUDYLINE. **IV.** I. M. GOLDBERG (Acta med. scand., 1935, **85**, 136—146, 147—153).—III. Solutions of Cu salts irradiated with ultra-violet light stimulate hæmatopoiesis in normal rabbits. Irradiated Cu and Fe salt solutions administered parenterally accelerate regeneration of blood after experimental hæmorrhagic anæmia.

IV. Irradiated Cu and Fe solutions depress the local anaphylactic reactions but apparently do not affect the course of anaphylaxis. R. N. C.

Effects of β-rays from radium on the agent of the Rous sarcoma, on bacteriophage, on tetanus toxin, and on certain bacteria, antibodies, and enzymes. S. L. BAKER (Brit. J. Exp. Path., 1934, **16**, 148—155).—The relative susceptibility to destruction by β-rays is examined. The agent of Rous sarcoma is not of an enzymic character. CH. ABS. (*p*)

Effect of ultra-violet light irradiation on carbohydrate metabolism. I. Changes of blood-sugar and blood-diastase after total irradiation from the noonday sun. A. MARCHIONINI and C. HÖVELBORN (Klin. Woch., 1935, **14**, 1387—1392).—The fasting blood-sugar val. in man is sometimes depressed and blood-diastase raised by total ultra-violet irradiation, suggesting a relation between skin-function and insulin output. R. N. C.

Reduction and oxidation by ultra-violet irradiated sugar.—See this vol., 1094.

Heliotropism of cholesterol. A. H. ROFFO (Strahlenther., 1935, **53**, 317—325; Chem. Zentr., 1935, ii, 2828).—The appearance of tumours as a result of irradiation with light of λ 180—340 mμ is preceded by local increase of blood-cholesterol. R. N. C.

Biological assay of hydrastine, berberine, and their mixtures by the isolated intestine. F. MERCIER (Compt. rend. Soc. Biol., 1936, **122**, 965—968). H. G. R.

Biological assay of liquid extracts of *Hydrastis*. F. MERCIER and L. VIGNOLI (Compt. rend. Soc. Biol., 1936, **122**, 968—970). H. G. R.

Recent advances in enzyme chemistry. E. WALDSCHMIDT-LEITZ (Chem. and Ind., 1936, 620—626).—A lecture.

Borders of physics and biology. C. E. GUYE (Arch. Sci. phys. nat., 1936, [v], **18**, 154—171).—Probability considerations are discussed in relation to mol. theories of life. Thermal agitation alone is insufficient to account for the appearance of high degrees of asymmetry in mols. of high mol. wt. F. A. A.

Reversible enzymic oxidation of *d*-glucoascorbic acid. S. S. ZILVA (Biochem. J., 1936, **30**, 1215; cf. A., 1934, 707).—The enzyme from apples which dehydrogenates *l*-ascorbic acid also reversibly dehydrogenates *d*-glucoascorbic acid at p_H 4·4 and room temp. W. McC.

Lactic dehydrogenase of animal tissues. D. E. GREEN and J. BROSTEAUX (Biochem. J., 1936, **30**, 1489—1508).—With enzyme–co-enzyme–lactate-carrier systems, the product of oxidation, $AcCO_2H$, inhibits almost completely the oxidation of lactate, but in presence of KCN or NH_2OH the oxidation proceeds linearly for a long time. The enzyme is very sensitive to p_H, and is associated with the enzymes oxidising malate, fumarate, and β-hydroxy-propionate and -butyrate. It catalyses the oxidation of *l*-lactate, whilst *d*-lactate, lactamide, and *iso*serine are not oxidised. It can be determined in the tissues of pigeons, rabbits, and rats, and H_2O-clear solutions can be prepared with Q_{O_2} of 400—500. Very small amounts of lactate are not oxidised with an appreciable velocity, and there is no crit. concn. of co-enzyme below which the rate of oxidation of lactate falls sharply. The co-enzyme is reduced by $Na_2S_2O_4$ or by the enzyme system, and when reduced is unstable in acid, but not in alkaline, solution. The co-enzyme is a sp. carrier between lactic acid and the O carrier, and cannot be replaced by the co-enzyme of hexose monophosphate dehydrogenase. Flavin, adrenaline, and, to a slight extent, yellow pigment can act as carriers, but ascorbic acid, cytochrome, and glutathione are inactive. A new classification of dehydrogenase systems is given. J. N. A.

Components of dehydrogenase systems. XII. Mechanism of dehydrogenation of alcohol and of triose phosphates. Mechanism of oxidation–reduction. H. von Euler, E. Adler, and H. Hellström (Z. physiol. Chem., 1936, **241**, 239—272; cf. this vol., 519).—EtOH in presence of its sp. apodehydrogenase reversibly converts cozymase (I) into dihydrocozymase (II), an equiv. amount of EtOH being converted into MeCHO. (II) exhibits an absorption max. at 340 mμ, is stable in alkaline and slightly acid media (rapidly destroyed at p_H 3) and to heat at p_H 7·6, and is re-oxidised by flavin enzyme. The point of equilibrium in the reaction (I)$\rightleftharpoons$(II) favours formation of (I) and *K* increases as p_H decreases. Reversible reduction of (I) with $Na_2S_2O_4$ at p_H >8 and with Zn in 0·1*N*-NaOH at 0° yields a yellow product exhibiting absorption max. at 360 mμ. This product reduces methylene-blue and $AgNO_3$, is not inactivated by acid, but loses its colour on neutralising, and is rapidly inactivated by heat. Dihydroxyacetonephosphoric acid is dehydrogenated by a dehydrogenase from yeast with (I) acting as sp. co-enzyme. Since the H donator in the oxidation–reduction process of alcoholic fermentation is probably a triosephosphoric acid it follows that (I) acts as a H carrier, transferring H to MeCHO. W. McC.

Dehydrogenase systems in seeds of various plants. T. Thunberg (Lunds. Univ. Arsskr., 1934, II, **30**, No. 13, 44 pp.).—The enzyme occurs in widely varying amounts in certain seeds. Ch. Abs. (*p*)

Allantoinase in insects. M. L. Rocco (Compt. rend., 1936, **202**, 1947—1948).—Aq. extracts of many winged insects when incubated at 39—40° contain allantoic acid enzymically derived from allantoin. J. L. D.

Reduction of biliverdin to bilirubin in tissues. R. Lemberg and R. Wyndham (Biochem. J., 1936, **30**, 1147—1170).—Biliverdin (I) is reduced anaërobically by guinea-pig's tissues (liver, kidney, spleen, brain, lung, muscle, blood, and heart, but not skin) and aërobically by the liver, spleen, kidney, and brain. The liver of man, horse, cat, rat, mouse, fowl, pigeon, *Echidna*, and (less powerfully) frog also reduce (I). Dehydrogenase systems and ascorbic acid in guinea-pig's liver reduce (I). Aldehydes (II), lactate, EtOH, citrate, formate, and (less effectively) succinate act as H donators in presence of liver enzymes. Glucose (III) dehydrogenase also reduces (I) slightly but most of the activity of (III) is due to glycolysis. (II) are activated by proteins and by an aldehyde dehydrogenase (probably not xanthine oxidase), and the other substrates by their sp. dehydrogenases. With MeCHO activated by protein the system is stable to heat and acts much more rapidly on (I) than on methyleneblue. (I) and mesobiliverdin are reduced in a few min. to the corresponding rubins by Zn in aq. NH_3 in absence of O_2. W. McC.

Enzymic degradation of starch.—See this vol., 1096.

Amylase during the growth and ripening of grains. T. Chrząszcz and J. Janicki (Biochem. J., 1936, **30**, 1298—1302).—All three amylolytic functions (liquefying, dextrinising, and saccharifying) appear in the forming grain of barley, wheat, and oats immediately after flowering. The subsequent decrease in activity is antagonised by peptone or dil. NaCl solutions. H. D.

Amylosynthease. XXV. Zymogen of yeast amylosynthease. XXVI. Zymogen of higher plant amylosynthease. Distribution in higher plants which accumulate starch. XXVII. Amylosynthease of higher plants which accumulate starch. XXVIII. Reaction velocity of amylosynthease. T. Minagawa (J. Agric. Chem. Soc. Japan, 1935, **11**, 370—373; cf. A., 1935, 1162).—XXV. Yeast extract, after treatment with papain and filtration, contained amylosynthease (I). The latter was originally present as zymogen (II). Aq. Na_2SO_4, K_2SO_4, KCl, and NaCl extract (II) but not (I).

XXVI. (I) was extracted from higher plants by means of papain. It occurs in many seeds (notably rice) and in tubers of potato and *Sagittaria sagittifolia*.

XXVII. (I) occurs mainly in the endosperm of rice. The embryo contains amylase (III). Samples from glutinous rice differed from yeast-(I) in being sol. in glycerol but not in $COMe_2$ and inactivated by H_2S, $HgCl_2$, and $Pb(OAc)_2$.

XXVIII. (I) from rice showed optimum activity at 35—46° and p_H 6·0—6·4 according to the substrate used. (I)–(III) mixtures showed antagonistic actions. Ch. Abs. (*p*)

(a) **Mechanism of production of a specific bacterial enzyme which decomposes the capsular polysaccharide of type III pneumococcus.** R. Dubos. (b) **Use of graded collodion membranes for the concentration of the enzyme.** R. Dubos and J. H. Bauer (J. Exp. Med., 1935, **62**, 259—269, 271—279).—(a) The micro-organism effecting decomp. of the polysaccharide produces the enzyme when grown on the sp. substrate, but not when grown on a casein hydrolysate medium. The yield of enzyme is dependent on the concn. of polysaccharide present and on the no. of cells used as inoculum. The enzyme is not produced in the absence of cellular multiplication.

(b) The enzyme is associated with a protein, the separation of which by membrane filtration is described. Ch. Abs. (*p*)

Effect of hæmolytic substances on blood-catalase. A. Levi (Arch. Farm. sperim., 1936, **61**, 121—142).—The contents of red corpuscles, hæmoglobin (I), and catalase (II) in blood (rabbit) are diminished by intravenous injection of $KClO_3$ or Na_2TeO_3. Solanine and the venom of *Vipera aspis* decrease erythrocytes and, to a greater extent, (I) and (II). The level of (II) is related to the content of erythrocytes and pigments derived from (I). E. P.

Rôle of cozymase in phosphorylation in yeast systems. Å. LENNERSTRAND (Naturwiss., 1936, **24**, 462—463).—The cessation of O_2 uptake after a time in the system apozymase+glucose+hexose diphosphate (I)+cozymase (II)+pyocyanine (III)+phosphate buffer (p_H 6·2), its renewal on the addition of (II) or (I)+(II), and the fact that no inactivation of (II) takes place in the absence of F' and (III) are explained by the view that (II) is present in a higher and a lower and less stable phosphorylated condition. During fermentation the higher phosphorylated substance is formed from the lower with the PO_4''' set free from phosphorylated C_3 compounds. In presence of F', however, the additional PO_4''' can only come from (I), and this reaction, being slower than the preceding one, leads to inactivation of (II). A. L.

Cozymase. X. Phosphatase and cozymase. K. MYRBÄCK and B. ÖRTENBLAD. **XI. Reducing group of cozymase.** K. MYRBÄCK (Z. physiol. Chem., 1936, **241**, 148—155, 223—232; cf. A., 1935, 1278).—X. The inactivating effect of ordinary kidney- and bone-phosphatase (I) on cozymase (II) is not due to (I) itself but to an accompanying enzyme. The purity of (II) cannot be satisfactorily determined with apozymase (III) because of alterations in (III) on keeping.

XI. In its behaviour towards HOI, Hagedorn and Jensen's reagent, and Mg+H_2SO_4, (II) closely resembles ouabain and the lactone of angelic acid (cf. Thiele *et al.*, A., 1902, i, 155). W. McC.

Composition of cozymase. H. VON EULER and F. SCHLENK (Svensk Kem. Tidskr., 1936, **48**, 135—137).—The empirical formula of highly purified cozymase is $C_{21}H_{27}O_{14}N_7P_2$, in agreement with its being made up of 1 mol. each of adenine and nicotinamide and 2 mols. of pentose phosphate. Its chemical properties can be interpreted in terms of this structure. E. A. H. R.

Inhibition of the action of Schardinger's enzyme by co-enzymes containing adenine. B. ANDERSSON (Z. physiol. Chem., 1936, **241**, 11—16; cf. A., 1935, 1414).—Adenine and substances of which it is a constituent [adenosine > adenylic acid (I) > adenosinediphosphoric acid (II) and adenyl pyrophosphate, cozymase (III), and Warburg's co-enzyme] restrict in varying degrees the action of the enzyme. The effect produced by (I) and (II) is not altered following treatment with dil. aq. NaOH but that of (III) is greatly increased, the increase not being due to liberation of (I) or of $H_4P_2O_7$. $Na_4P_2O_7$ has no inhibitory effect and nicotinamide only a slight effect. NaOH probably causes rearrangement of the (III) mol. and since no acid OH is thus liberated a formula for (III) similar to that of Barrenscheen is to be preferred to that of Lohmann. W. McC.

Intermediate metabolism and oxidation processes. I. Co-enzyme and intermediate carbohydrate metabolism. A. UTEVSKI (Ukrain. Biochem. J., 1932, **5**, 71—86).—In presence of washed muscle tissue, glycogen, glucose, fructose, and glycerol do not yield MeCHO (I) but pyruvate (II) is decarboxylated. The addition of boiled muscle juice (III) restores the power to produce (I) and also to oxidise (II). The conversion of fumaric into malic acid is effected by washed muscle tissue, but the further metabolism of malic acid proceeds normally only when (III) is added. Probably a co-enzyme essential in intermediate metabolism is present in (III). W. O. K.

Action of dyes on enzymes. Nature of the union between yeast invertase and sucrose. J. H. QUASTEL and E. D. YATES (Enzymologia, 1936, **1**, 60—80).—The reversible inactivation of invertase by acid (I) and basic dyes (II) has been interpreted quantitatively in terms of the mass action law. Variation of dye, sucrose, and $[H^{\cdot}]$ indicates a reaction between (I) ion and (II) ion and positive and negative ions of the enzyme, respectively. Glucose competes mainly with (II), fructose with (I), and sucrose with both (I) and (II). Reduced dyes are usually less toxic. E. D. Y.

Swedish top yeast: carboxylase. K. WÜLFERT (Tids. Kjemi, 1936, **16**, 77—79, 82—86).—To obtain high carboxylase (I) activity, the yeast to be dried must be very fresh. Extracts of the dried yeast give vals. for Neuberg's const. <1, in agreement with theory. The effects on the (I) activity of dried yeast of warming, addition of sugars, autolysis, plasmolysis, and poisoning with PhMe or $CHCl_3$ have been studied. M. H. M. A.

β-Glucosidase from *Sorghum saccharatum*. C. ANTONIANI (R. Ist. lombardo Sci. Lett. Rend., 1935, **68**, 355—362; Chem. Zentr., 1935, ii, 2683—2684).—The enzyme from ungerminated seed shows optimum activity at p_H 4·6 and, unlike the β-glucosidase from bitter almonds and malt, decomposes cellobiose and salicin at approx. the same rates. Hydrolysis of salicin is inhibited by glucose but not by galactose. The enzyme does not decompose lactose and contains no β-galactosidase. A. G. P.

Synthetic action of β-glucosidase on glucose. I. VINTILESCO, C. N. IONESCO, and A. KIZYK (Bul. Soc. Chim. România, 1935, **17**, 283—292).—The amount of α-glucose in the α–β equilibrium mixture is increased by increasing the concn. or by adding $COMe_2$. Changes in [α] of glucose (I) treated with emulsin in H_2O and aq. $COMe_2$ and the further change on destruction of the (I) by yeast show that the synthesis of gentiobiose from 2 mols. of β- and of cellobiose from 1 mol. of β- and 1 mol. of α-glucose follow the law of mass action. Increase in the amount of α-form favours the formation of cellobiose, in accordance with expectation. R. S. C.

Biochemical synthesis of β-glucosides derived from alcohols immiscible with water. I. VINTILESCO, C. N. IONESCO, and M. SOLOMON (Bul. Soc. Chim. România, 1935, **17**, 267—281).—A solution containing n-C_6H_{13}·OH (30), H_2O (19·2), $COMe_2$ (51·9), and glucose (1·5%) with emulsin (I) (0·5 g. per

100 c.c.) gives β-n-*hexylglucoside*, m.p. 87—89°, $[\alpha]_D^{20}$ −33·28° in H_2O, hydrolysed by (I) or dil. acid. The above proportions are shown to be the optimum by a study of the solubility relations of the quaternary system. R. S. C.

Serum-lipase during naphthalene ocular lesions in rabbits and its probable rôle in the pathogenesis of senile cataract. D. Michail and I. Pacurariu (Compt. rend. Soc. Biol., 1936, **122**, 1125—1128).—Serum-lipase is lowered during $C_{10}H_8$ intoxication with the appearance of ocular symptoms, reaching a min. when the opacity becomes total. The val. then slowly (4—5 months) returns to normal. H. G. R.

Deaminating enzyme of flesh-fly larvæ. A. W. A. Brown and L. Farber (Biochem. J., 1936, **30**, 1107—1118).—The deaminase activity of extracts of the larvæ of *Lucilia sericata* and *Calliphora erythrocephala* is max. at p_H 7·6, is greater under anaërobic than under aërobic conditions, and increases linearly with temp over the range 10—37·5°. The extracts do not deaminise NH_2-acids or di- or tri-peptides but attack the higher hydrolytic products of protein; they possess proteinase, poly- and di-peptidase, uricase, and slight deaminase activities. W. O. K.

Proteolytic enzymes. IX. Inactivation of papain with iodine. M. Bergmann and L. Zervas. **X. Enzymes of papain and their activation.** M. Bergmann and W. F. Ross (J. Biol. Chem., 1936, **114**, 711—715, 717—726).—IX. HCN does not affect the specificity of papain towards benzoyl*iso*glutamine (I), but it increases the amount of active enzyme, and thus accelerates the cleavage of (I). Inactivation of papain with I extends not only to cleavage of gelatin and acylated peptides, but also to free peptides. Reactivity can be regenerated by HCN, but it is always < that of the original papain. The loss of activity is more pronounced in the case of substrates with a small cleavage rate.

X. Hydrolysis of (I) by HCN–papain is completely suppressed by small amounts of $NHPh\cdot NH_2$ (II), but (II) has no effect on the hydrolysis of peptone from albumin. HCN-activated papain consists of two distinct enzymes, papain peptidases I and II. Peptidase I is inhibited by (II) and very probably contains a CHO group, whilst peptidase II is unaffected by (II) and is reversibly inactivated by I. Peptidase I is the first proteolytic enzyme of known specificity which requires neither terminal NH_2 nor CO_2H, and is thus an endopeptidase, in distinction to an exopeptidase which requires a terminal peptide linking. It is influenced by the nature of the NH_2-acid forming or lying near the ·CO·NH· group which is hydrolysed. It is suggested that in natural papain there is an equilibrium between the peptidases I and II and a compound of these. J. N. A.

Enzymic histochemistry. XXI. Proteolytic enzymes of the larvæ of clothes- and wax-moths. F. Duspiva (Z. physiol. Chem., 1936, **241**, 177—200; cf. this vol., 244, 759).—Larvæ of *Galleria mellonella* cannot digest keratin (I). In the intestinal juice the proteinase (II), which is the most active enzyme present, exhibits optimal action [on caseinogen (III)] at p_H 9·6. In *Tineola biselliella* the val. is 9·3 and the amount of (III) digested $\propto$ the amount of (II). In both species the optimal p_H for the aminopolypeptidase action (on alanylglycylglycine) is 8·1 and those for the dipeptidase action (on alanylglycine) are 7·5 (*Tineola*) and approx. 7·8 (*Galleria*). The peptidases are equally sensitive to the action of ·SH compounds [*e.g.*, thioglycollic acid (IV)], but whereas (II) of *Tineola* is unaffected by low concns. of (IV), the action of (II) of *Galleria* is restricted. The ability of insects to utilise (I) is due entirely to the existence of a negative oxidation–reduction potential in their intestinal juice. W. McC.

Proteases of acid proteolytes. M. E. C. Gorini and L. Gorini (R. Ist. lombardo Sci. Lett. Rend., 1935, **68**, 115—125; Chem. Zentr., 1935, ii, 2964).—Enzymic activity in filtered solutions increases with the age of the culture from which it is obtained. Best results were obtained with 24-hr. cultures. Citrate additions have a favourable effect. Activity is max. at p_H 7·0 and ceases at 4·3. A. G. P.

Digestive enzymes in marine invertebrates. II. Proteolytic enzymes in the starfish, *Distolasterias nipon*, Döderlein. E. Sawano (Sci. Rep. Tokyo Bunrika Daigaku, 1936, **2**, B, 179—199; cf. this vol., 521).—Extracts of the stomach of *D. nipon* hydrolyse glycylglycine (I) but not gelatin; those of the pyloric cæcum hydrolyse proteins, peptones, and (I) and contain (as does the rectal gland) a cathepsin-like enzyme and a trypsin-like carboxypolypeptidase accelerated by cystine and inhibited by cysteine. Optimum p_H vals. are given for various substrates. F. O. H.

Location of the anti-enzyme in egg-white. J. S. Hughes, H. M. Scott, and J. Antelyes (Ind. Eng. Chem. [Anal.], 1936, **8**, 310—311).—The antiproteolytic enzyme in new-laid eggs is chiefly located in the inner thin white. S. C.

Alcohol and peptic digestion. E. Trabucchi (Arch. Farm. sperim., 1936, **61**, 186—208).—The inhibition by EtOH of *in-vitro* proteolysis by pepsin is due not merely to inactivation of the enzyme but to modifications of the physico-chemical properties of the substrate, *e.g.*, diminution of dissociation and of enzyme–substrate adsorption, increase in η, and, particularly, inhibition of preliminary swelling (due to dehydration by EtOH) of substrate necessary for subsequent hydrolysis. F. O. H.

Inactivation of crystalline pepsin. J. Steinhardt (Nature, 1936, **138**, 74—75).—At p_H vals. $\not>$ 6·45, cryst. pepsin inactivates unimolecularly at a rate $\propto 1/[H^{\cdot}]^5$. Equilibria governing the concn. of an unstable species of pepsin ion, formed by dissociation of five acidic groups, probably determine the rate. Between ionic strengths of 0·012 and 0·10, the velocity at const. p_H increases by > 30 times. On agitation, a heterogeneous reaction, independent of p_H and ionic strength over wide limits, obscures the results. L. S. T.

Phosphatase distribution in higher plants. V. Ignatieff and H. Wasteneys (Biochem. J., 1936, **30**, 1171—1182).—The phosphatase contents of various parts of bean, potato, radish, and wheat plants at different stages of development have been determined. W. McC.

Phosphatase of potato and sugar-beet. E. Pfankuch (Z. physiol. Chem., 1936, **241**, 34—46; cf. A., 1935, 1181).—The phosphatase (I) content of the press-juice from potatoes is $\gg$ that of any other vegetable material. (I) is non-sp. but hydrolyses substrates at different rates (Na inositol hexaphosphate : Na hexose diphosphate : Na α-glycerophosphate : Na phosphoglycerate : Na β-glycero-phosphate as 23 : 52 : 61 : 66 : 100). The action of (I) (optimal at p_H 5·8—5·9) is easily inhibited by PO_4''' and very easily by NaF, which acts more powerfully with high substrate concn. Inhibition is also caused by org. and inorg. anions and cations, $Cu^{\cdot\cdot}$ being especially powerful. The effect of $Cu^{\cdot\cdot}$ is counteracted by CN′ and glutathione (II) and partly counteracted by ascorbic acid (III) although (II) and (III) alone have no effect on (I). $Mg^{\cdot\cdot}$ does not activate (I). W. McC.

Serum-phosphatase in the domestic fowl. R. H. Common (J. Agric. Sci., 1936, **26**, 492—508).—The serum-phosphatase (I) of laying hens was > that of cocks and pullets. Vals. for hens altered very little during periods of suspended egg-production. In chicks, (I) increased rapidly until 10—12 days after hatching, and subsequently fell sharply to a lower level at 3 weeks. Thereafter vals. for male birds declined steadily until maturity, those for females being of a similar order until increasing again at the onset of laying. Variations for laying birds were not decreased in range by administration of Radiostol (3000 international units of vitamin-*D* per ml.). In pullets the increase in (I) vals. on a low-Ca ration was $\gg$ when $CaCO_3$ supplements were fed. A. G. P.

Brain phosphatase. K. V. Giri and N. C. Datta (Biochem. J., 1936, **30**, 1089—1096).—The phosphatase activity of aq. extracts of $COMe_2$-treated brain tissue is max. at p_H 5·0 and 9·4—9·6, indicating that two distinct phosphatases are present. Their ratio is approx. const. for brains of animals of the same species. Both hydrolyse hexose diphosphate more rapidly than β-glycerophosphate. Purification of the enzymes may be effected by isoelectric pptn. of the inert material at p_H 4·8, dialysis, ultrafiltration through Cellophane membranes, and $COMe_2$ pptn. $Mg^{\cdot\cdot}$ activates the enzyme in alkaline but not in acid solution, the activation being enhanced when preps. are purified by dialysis. The rate of hydrolysis by either phosphatase is initially linear irrespective of the purity of the enzyme and presence or absence of Mg, but depends on the concn. of substrate. W. O. K.

Enzymes in cancer. II. Glycerophosphatases of human erythrocytes. J. W. Schoonover (Biochem. J., 1936, **30**, 1097—1106).—Hæmolysates of normal and cancerous erythrocytes hydrolyse α- and β-glycerophosphate optimally at p_H 5·6, the rate being about 6 times as great for α as for β. Hydrolysis is more rapid in presence of $Mg^{\cdot\cdot}$, but the effect with β is relatively > that with α and less evident with cancerous than with normal erythrocytes. The β-glycerophosphatase activity of erythrocytes is relatively const. in normal but often increased in cancerous individuals. The α-glycerophosphatase activity is less const. in normals and is not significantly increased in cases of cancer. W. O. K.

Effects of activators, inhibitors, and destructive agents on urease. T. Bersin and H. Koster (Z. ges. Naturwiss., 1935, **1**, 230—242; Chem. Zentr., 1935, ii, 2965).—Active urease (I) is a ·SH compound. Glutathione and $K_2S_2O_5$ at p_H 7·16 increase the activity of soya-bean preps. The latter are hydrogenated by succino-dehydrogenase. In plants the dehydrogenase regulates the activity of (I). Effects of various As and Se compounds and of $CH_2I{\cdot}CO_2'$ are examined. Ascorbic acid alone has no effect on (I), but in presence of Fe is injurious. A. G. P.

Reaction of iodoacetate and of iodoacetamide with various thiol groups, with urease, and with yeast preparations.—See this vol., 1074.

Diastase determination in blood. II. F. Baltzer (Klin. Woch., 1935, **14**, 1395—1397; Chem. Zentr., 1935, ii, 2854; cf. this vol., 747). H. N. R.

Yeast grown in cyanide. II. L. B. Pett (Biochem. J., 1936, **30**, 1438—1445; cf. A., 1935, 1165).—Yeast cultured in the presence of CN′ differed from top and bottom yeast in its respiration and fermentation properties, having a high flavin (I) content, exhibiting no Pasteur reaction or CN′ inhibition. Prolonged sub-culturing in CN′ media gave a yeast with no (I) but containing a blue fluorescing pigment. H. D.

Comparative effects of the elements on the growth of *Aspergillus niger* (stimulation and toxicity). K. Pirschle (Planta, 1935, **24**, 649—710).—The toxicity of Fe^{III}, Ce^{IV}, and Hg^{II} salts is > that of the corresponding Fe^{II}, Ce^{III}, and Hg^{I} salts, respectively. The very toxic action of $Fe(CN)_6''''$ and $Fe(CN)_6'''$ is not due to the formation of CN′. Ni^{II} exhibits greater toxicity and stimulative effects than Co^{II}. Metals of the Pt group show progressively varying effects according to their position in vertical or horizontal series. The indispensability of Mn is questioned, although its stimulative action is very marked. In general elements in anionic forms are usually more toxic than in cationic forms (exception, uranyl salts more toxic than uranates). The following relative toxicities are established: $S_2O_4''>S''>SO_3''=S_2O_8''>SO_4$; $TeO_3''>TeO_4''$; $SeO_3''>SeO_4''$; $AsO_3'''>AsO_4'''$; $SeO_4''>TeO_4''>SO_4''$; $SeO_3''>TeO_3''>SO_3''$; $CrO_4''>MoO_4''>SO_4''$; $AsO_4'''>SbO_4'''>PO_4'''$. Stimulative effects are in the relative order Zn>Cd>Hg; Ge>Sn>Pb; Al>Y>La; Si>Ti; P>As; P>V; S>Se; S>Cr. A. G. P.

Effect of zinc on the metabolism of *Aspergillus niger*. G. M. Vassiliev (Arch. Mikrobiol., 1935, **6**, 250—275).—Zn affects the growth of *A. niger* and also its metabolism. In the latter respect Zn acts principally on the course of formation and consumption of intermediate products of sugar metabolism and of gluconic (I) and citric (II) acids. With strains producing (I), or (I) and (II), Zn decreases the production of the acids, but with (II)-producing strains, acid accumulation is favoured. Zn affects metabolism not by direct action on the protoplasm, but indirectly as a result of its influence on vegetative growth. It does not modify the respiration of the mould. A. G. P.

Acids and alcohols as nutrients for *Monascus*. K. Sato and I. Naito (J. Agric. Chem. Soc. Japan, 1935, **11**, 473—479).—*M. anka* assimilated citric, fumaric, gluconic, lactic, malic, and succinic acids, but not AcOH, $H_2C_2O_4$, kojic or tartaric acids. Suitable acids and alcohols were as effective as glucose as C sources. Ch. Abs. (*p*)

Fermentation of arabinose and fucose by *Aspergillus oryzæ*. II. T. Tadokoro (J. Agric. Chem. Soc. Japan, 1935, **11**, 365—369; cf. this vol., 639).—Arabinose yielded CO_2, HCO_2H (I), citric and glycollic (II) acids with smaller amounts of $H_2C_2O_4$ and kojic acid and glyceraldehyde. From fucose, (I), (II), and lactic acid were produced. MeCHO, $COMe_2$, EtOH, and AcOH were not obtained from either sugar. Ch. Abs. (*p*)

Formation of *d*-fructose from mannitol by means of *Penicillia*. A. Angeletti (Annali Chim. Appl., 1936, **26**, 234—236).—*d*-Fructose is produced from mannitol by the action of *P. crustaceum* (L.), Fries, and *P. luteum purpurogenum* after 20 days' fermentation. L. A. O'N.

***Rhizopus*. I. Production of *d*-lactic acid.** G. E. Ward, L. B. Lockwood, O. E. May, and H. T. Herrick (J. Amer. Chem. Soc., 1936, **58**, 1286—1288).—*R. oryzæ, arrhizus*, and *tritici* produced 19—62% of lactic acid (I) on a medium containing glucose, nutrient salts, and $CaCO_3$. Some strains produced little (I). In absence of $CaCO_3$ and with urea as N-source, *R. nigricans* (1 strain) and *chinensis* formed appreciable quantities of EtOH. H. B.

Assimilation of nitrites by fungi. I*a*, II. K. Sakaguchi and Y. Wang (Bull. Agric. Chem. Soc. Japan, 1936, **12**, 59—62, 63—69; cf. A., 1934, 1405).—I*a*. Using $NaNO_2$ in place of $NaNO_3$ in the Czapek medium, the classification of black *Aspergilli* has been studied. They can be divided into three groups.

II. *A. oryzæ*, *A. aureus*, and *A. batatæ* (but not *A. oryzæ*, Takahashi) convert $NaNO_3$ into $NaNO_2$, but neither is produced from NH_4Cl by *A. oryzæ*. $NaNO_2$ is assimilated selectively by all three species in presence of $NaNO_3$, which is attacked only after complete utilisation of $NaNO_2$. $NaNO_2$ and NH_4Cl are used up nearly at the same rate, and $NaNO_2$ is regarded as an intermediate in the resorption of $NaNO_3$ by moulds. A method for the determination of NO_2' in presence of NO_3' is described. J. N. A.

Chemistry of growth substance *B*. N. Nielsen and V. Hartelius (Nature, 1936, **138**, 203).—The growth substance previously described (A., 1933, 638) is produced when sucrose is inverted by means of org. or inorg. acids. Glycollic (I)+pyruvic acid (II) together act as growth substances for *Aspergillus niger*, but alone have little or no effect. Glyoxylic acid (III) alone, and (III) or ascorbic acid added to (I)+(II), have a similar effect. Oxidation with $KMnO_4$ or H_2O_2 destroys the growth substances which act on yeast, but not those which act on moulds. L. S. T.

Metabolic products of *Aspergillus terreus*, Thom. Geodin and erdin.—See this vol., 1116.

Ravelenin, a metabolic product of *Helminthosporium Ravenelii*, Curtis, and of *H. Turcicum*, Passerini.—See this vol., 1121.

Reactions of *Helvella*. II. G. Reif (Z. Unters. Lebensm., 1936, **71**, 435—442; cf. A., 1935, 1181).—The substance present in *H. esculenta* which reduces SeO_2 to Se is removed from aq. alkaline solution by distillation or by extraction with Et_2O or $CHCl_3$. The distillate gives a violet colour with a phosphotungstic–phosphomolybdic acid reagent, and, in acid solution, with fuchsin–SO_2 reagent. With the exception of that from *H. crispa*, no other fungus distillate gives these reactions. The SeO_2–H_2SO_4 reagent may be used to differentiate aldoses and ketoses. E. C. S.

"Tryptone" medium for detection of flat-sour spores. O. B. Williams (Food Res., 1936, **1**, 217—221).—Plate counts with a casein digest medium give better results than with other solid media or dilution methods with liquid media. Low-resistant spores are destroyed by 5 min. boiling, but resistant forms are not destroyed by 30 min. boiling. E. C. S.

Growth-promoting activity of certain sterols on *Trichomonas columbæ*. R. Cailleau (Compt. rend. Soc. Biol., 1936, **122**, 1027—1028).—The activity of cholesterol, modified in either the cyclic portion or the side-chain, is described. H. G. R.

Effect of emetine on *Endamœba histolytica* in culture. J. H. St. John (Amer. J. Hyg., 1933, **18**, 414—432).—Lethal dosages are examined in relation to lethal time. Ch. Abs. (*p*)

Chemotherapy of experimental trichiniasis. D. N. Greenwood (J. Chemother., 1935, **12**, 232—234).—Tartar emetic, acetarsone, emetine, parathormone, Ca gluconate, and viosterol were without parasiticidal action and did not increase calcification of the cyst wall or of trichinellæ. Ch. Abs. (*p*)

Function of protohæmin in protozoa and parahæmotropic bacteria. A. Lwoff (Compt. rend. Soc. Biol., 1936, **122**, 1041—1042).—In presence of cytochrome-*c*, only 2/3 of the protohæmin is transformed into hæmin-*c*. H. G. R.

Acetic bacteria produced in Formosa. VI. S. Tanaka (J. Agric. Chem. Soc. Japan, 1935, **11**, 435—455).—Organisms from fruit, saké, etc. are examined. Ch. Abs. (*p*)

Relation between iron and oxidase reaction. Bacillus occurring in mussels at the bottom of a mussel-hill of the later stone age. R. Katsunuma (Z. Klin. Path. Hämatol. Japan, 1933, **2**, 1).—Bacteria which could be cultivated repeatedly on an Fe-free medium are described. A slow decline occurs in oxidase activity of successive generations. Ch. Abs. (*p*)

Bacteriological and biochemical relationships in the *pyocyaneus–fluorescens* group. I. Chro-

mogenic function in relation to classifications. G. E. Turfitt (Biochem. J., 1936, **30**, 1323—1328).—Media are elaborated on which the *pyocyaneus–fluorescens* group of bacteria exhibit a marked constancy in pigment production, and evidence is obtained for the classification of these organisms into a single genus on the basis of their chromogenic function. P. W. C.

Pigments of purple bacteria. I. Spirilloxanthin, a component of the pigment complex of *Spirillum rubrum*. C. B. van Niel and J. H. C. Smith (Arch. Mikrobiol., 1935, **6**, 219—229).—The isolation of *spirilloxanthin*, $C_{48}H_{66}O_3$, is described. It is a purple pigment, highly unsaturated (15 double linkings), contains $\not>$ one OH, and no free $\cdot CO_2H$. Other carotenoid pigments are also present in the organism. A. G. P.

Nodule bacteria. IX. Electrical properties of the accessory substance. A. Itano and A. Matsuura (J. Agric. Chem. Soc. Japan, 1936, **12**, 457—466; cf. this vol., 899).—Extracts of bean nodules in hot and cold H_2O, and EtOH+hot H_2O, were dialysed and compared with a yeast extract. The accessory substance was found mainly in the cathode chamber. The yeast extract was inert towards electrodialysis. There was no relation between the accessory substance and N content. J. N. A.

Anaërobic bacteria. VI. Nature and systematic position of a new chromogenic *Clostridium*. E. McCoy and L. S. McClung. **VII. Serological relations of *Cl. acetobutylicum*, *Cl. felsineum*, and *Cl. roseum*.** L. S. McClung and E. McCoy (Arch. Mikrobiol., 1935, **6**, 231—238, 239—249; cf. B., 1935, 476).—VI. The pigmentation, biochemical, and agglutination activities are recorded.

VII. Antigenic differences and relationships are examined. A. G. P.

Effect of concentration of sorbitol on production of sorbose by the action of *Acetobacter suboxydans*. E. I. Fulmer, J. W. Dunning, J. F. Guymon, and L. A. Underkofler (J. Amer. Chem. Soc., 1936, **58**, 1012—1013).—The rate of production and the final yield of sorbose (I) from sorbitol (II) and *A. suboxydans* (which is much superior to *A. xylinum*) increase with rise in the surface–vol. ratio. For a given ratio the yield of (I) is a linear function of log *t* up to 80%. With concns. of (II) <40%, rate of production is decreased by increased concn. of (II), but the final yield is little affected. Little or no action occurs with concns. >40%. H. B.

Paracolon group of bacteria. B. R. Sandiford (J. Path. Bact., 1935, **41**, 77—78).—The organisms are coliform, but ferment lactose either atypically or not at all. They produce indole. Fermentation of rhamnose follows a course different from that commonly found in bacterial fermentations. Gases other than H_2 and CO_2 are probably produced. Ch. Abs. (*p*)

Growth of bacteria in media containing previously-heated ovalbumin as the source of nitrogen. E. Pozerski (Compt. rend. Soc. Biol., 1936, **122**, 909—911).—*B. coli* cannot utilise ovalbumin (deprived of peptone and coagulated at various temp.) as a sole source of N. H. G. R.

Hydrogen donators for *Proteus vulgaris*. D. Bach (Compt. rend. Soc. Biol., 1936, **122**, 1065—1067).—Alcohols, saturated aldehydes, and some org. acids (including NH_2- and unsaturated acids), but not unsaturated aldehydes, act as donators. H. G. R.

Development of the dehydrogenases of *Proteus vulgaris*. D. Bach (Compt. rend. Soc. Biol., 1936, **122**, 1068—1070).—The dehydrogenase activity decreases with the age of the culture; this is independent of the media, but in some cases this decrease is retarded. H. G. R.

Independence of the production of proteases and of the development of the cell of *B. prodigiosum*. W. Moycho (Compt. rend., 1936, **202**, 2007—2009; cf., A., 1928, 1402; this vol., 245).—Cultures in buffered 1% peptone media grow best at p_H 7·5. The proteolytic capacity increases with increasing acidity, allowance being made for diminished reproductive capacity, and is nil in feebly alkaline media. As $[PO_4''']$ decreases from *N*/8 to *N*/15, proteolysis increases but growth diminishes. J. L. D.

Streptococci producing a substance inhibiting growth of lactic streptococci. G. A. Cox and H. R. Whitehead (New Zealand J. Agric., 1936, **52**, 38—43).—The irregular occurrence in milk of streptococci, originating in dung, fodder, or the udder, which produce a substance inhibiting the growth of lactic streptococci is described. W. L. D.

Growth and metabolism of cells of *Streptococcus lactis* in sterilised milk (logarithmic phase). T. Matuszewski (Polish Agric. Forest. Ann., 1935, **34**, 403—455).—Lactic acid production per cell per hr. is determined for *S. lactis* and *S. cremoris*. Ch. Abs. (*p*)

Nutritive medium for the preparation of tuberculin. D. A. Zuverkalov and A. K. Sarkissov (Ann. Inst. Pasteur, 1936, **57**, 111—119).—After suitable hydrolysis a medium can be prepared from potato which will give a heavy growth of tubercle bacilli over a long period. The high buffering power maintains an optimal p_H for several months. The tuberculin prepared from potato broth produces no reaction in healthy animals, whilst the broth alone gives no reaction even in tuberculous animals and when conc. tenfold. P. G. M.

Influence of hæmoglobin on the virulence of tubercle bacilli. H. Porges (Wien. med. Woch., 1935, **85**, 1023—1024).—Hæmoglobin was without effect. A. G. P.

Spontaneous protein flocculation in old, acidified cultures of human *B. tuberculosis* in Sauton's medium and its acceleration by heat. F. van Deinse (Compt. rend. Soc. Biol., 1936, **122**, 1019—1020).—The pptn. occurs after 40 days at a $p_H \not> 6·6$. The ppt. firmly adsorbs tuberculin and may be redissolved in dil. alkali. It is also irregularly observed in bovine but never in avian cultures. H. G. R.

Action of poppy-seed oil, with and without added cholesterol, on staphylococcus toxin.

J. Schwartz (Compt. rend. Soc. Biol., 1936, **122**, 1006—1009).—The neutralising action of the oil is not observed when the former contains 3% of added cholesterol. H. G. R.

Bactericidal action of ethyl*apo*quinine and ethylhydrocupreine on type strains of pneumococci. I. *In vitro*. S. Matsuda (Japan. J. Med. Sci., IV; Proc., 1933, **7**, 45—47).—Ethyl*apo*quinine hydrochloride (I) inhibits types I, II, and III pneumococci in concns. of 1 in 2 million; optoquin (II) requires 1 in 512,000. As a bactericide (I) is 2—8 times as potent as (II). Type III pneumococcus was much more susceptible than type I or II. Ch. Abs. (*p*)

Changes produced in spirochætes of relapsing fever by action of pharmacological reagents. III. Effect of pyridine and its alkyl derivatives. K. Hoshina (Luea, Bull. Soc. Jap. Syphiligraph. Kyoto, **7**, 129—136).—The toxicity of 2-methyl-, 2 : 6- and 2 : 4-dimethyl-, and 1 : 4 : 6-trimethylpyridine increased with increasing length of the side-chain. Low concns. of the first three named caused an increase in mobility, the effect decreasing in the order given. Ch. Abs. (*p*)

Inhibitory power of the neutral sulphate of 8-hydroxyquinoline ("sunoxol") on tubercle bacilli in different media, particularly in homogeneous cultures. P. Courmont, A. Morel, L. Perrot, and F. Dénard (Compt. rend. Soc. Biol., 1936, **122**, 1110—1113).—The sulphate is a powerful antiseptic for the bacillus. H. G. R.

Inhibitory power of two derivatives of 8-hydroxy-6-methylquinoline on pathogenic bacteria. A. Morel, A. Rochaix, L. Perrot, and M. Moutou (Compt. rend. Soc. Biol., 1936, **122**, 1113—1114).—The hydrochloride is a powerful antiseptic, comparable with "sunoxol" (cf. preceding abstract), the action being only slightly affected by methylation of the Ph nucleus whereas it is markedly decreased by sulphonation. H. G. R.

Inhibitory power of derivatives of 8-hydroxyquinoline on pathogenic bacteria. A. Morel, A. Rochaix, L. Perrot, and A. Pegon (Compt. rend. Soc. Biol., 1936, **122**, 1115—1116).—The salicylate and sulphosalicylate are only slightly less antiseptic than "sunoxol" (I) (cf. preceding abstract) but are less caustic. The bacterial val. is decreased by sulphonation, but not to the same extent as with (I). H. G. R.

Action of ultra-violet light on bacteria. G. Dreyer and M. L. Campbell-Renton (Proc. Roy. Soc., 1936, B, **120**, 447—472).—The lethal effect of ultra-violet radiation on the 26 species and strains of bacteria tested is greatest for λ 2655, and 2536 > 2804 > 2482 > 2700. The bactericidal effect is not ∝ the relative energies of these λλ. The shape of the growth–exposure curve varies for different bacteria and between the strains of some bacteria, including some which are serologically alike. Sensitisation by erythrosin markedly increases the sensitivity to long λλ; the effect with shorter λλ varies widely. Gram-positive organisms show a much greater sensitivity to long λλ than do Gram-negative. The curves of sensitivity to various dilutions of disinfectants differ from each other and from the corresponding ultra-violet sensitivity curves. In the greater dilutions growth stimulation is observed. F. A. A.

Cholesterol and the lytic power of bacteriophage. B. S. Levin and I. Lominski (Compt. rend. Soc. Biol., 1936, **122**, 1063—1065).—The conc. bacteriophage is inhibited by large amounts of cholesterol (I), but when diluted is inhibited by a high and enhanced by a low concn. of (I). H. G. R.

Inactivation of crystalline tobacco-mosaic virus protein. W. M. Stanley (Science, 1936, **83**, 626—627).—Treatment of the active cryst. protein (A., 1935, 1181) with H_2O_2, CH_2O, HNO_2, or ultra-violet light produces inactive native proteins which, although slightly altered, retain certain chemical and serological properties characteristic of the virus protein. The inactive proteins do not produce the mosaic disease, or a protein of high mol. wt. on inoculation into Turkish tobacco plants, or local lesions in *Nicotiana glutinosa*, L. L. S. T.

Protective action of rabbit serum for vaccinia virus at high temperatures. E. W. Goodpasture and G. J. Buddingh (Science, 1936, **84**, 66—67).—Normal inactivated rabbit serum maintains the viability of vaccinia virus at 37° for longer times than do 50% glycerol, gum acacia, 3% mucin in saline, and sterile egg yolk. L. S. T.

New œstrogenic substance from ovaries. R. H. Andrew and F. Fenger (Science, 1936, **84**, 18—19).—Crystals, m.p. 95·1° (uncorr.), mol. wt. 320, of a *substance* (I), probably $C_{20}H_{41}O_2N$, which differs chemically and physiologically from urinary œstrogenic substances have been isolated from ovaries. 0·00001 mg. of (I) produces œstrus in rats after 96 hr. L. S. T.

Effect of ovarian extracts on oxygen consumption of the uterus. M. A. Khayyal and C. M. Scott (Quart. J. Exp. Physiol., 1935, **25**, 77—83).—Fresh follicular fluid from cows contains a substance (not œstrin or luteal hormone) which increases the rate of O_2 consumption of the isolated uterus of mice. The substance also occurs in human serum and is probably released from the ovary by the action of anterior pituitary hormones. Thyroxine also increases the O_2 consumption. Ch. Abs. (*p*)

Production *in vitro* of œstrogenic substances from organs. P. Rondoni, V. Carminati, and A. Corbellini (Z. physiol. Chem., 1936, **241**, 71—80).—Pulped horse liver containing 5% of added cholesterol yields œstrogenic material after being left for 5—6 weeks at 38—53°. W. McC.

Influence of œstrin injections on the balance between the prehypophyseal gonadotropic hormones of the rat. A. Lipschütz (Quart. J. Exp. Physiol., 1935, **25**, 109—120).—The action of œstrin is probably due to a change in the balance between the œstrogenic and luteinising hormones, the proportion of the latter being lowered. Spermatogenesis is usually disturbed. Ch. Abs. (*p*)

Testosterone, the crystalline male hormone from ox testes. K. David (Acta Brev. neerl.

Physiol., 1935, 5, 85—86; Chem. Zentr., 1935, ii, 3254; cf. A., 1933, 1033).—Testosterone forms an *acetate*, m.p. 140—141°, and an *oxime*, m.p. 221—222·5°. It is not acidic, and is saturated. The ultra-violet absorption spectrum is similar to that of cholestenone. Mild oxidation produces a diketone, m.p. 171—173°, with practically the same absorption spectrum, and probably identical with androstendione. R. N. C.

Characteristics of the testes hormone. K. Matsuzaki (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 140—142).—Injection of lipin fractions into normal and castrated male rats during 10 days caused hypertrophy of sex organs. Ch. Abs. (*p*)

Action of the male sex hormone preparation androstin in female hypertension. H. Mayrhofer (Wien. med. Woch., 1935, 85, 1038). R. N. C.

Assay of *trans*-dehydroandrosterone and its effects on male and female gonadectomised rats. V. Korenchevsky and M. Dennison (Biochem. J., 1936, 30, 1514—1522).—*trans*-Dehydroandrosterone (I) is a very weak sex hormone (rat unit approx. 940 $\times 10^{-6}$ g.). (I) shows some of the typical properties of the female hormones, and its restorative effect on the atrophied sexual organs of male and female gonadectomised rats is definite, but (except in the case of the preputial glands) small. The co-operative effect when injected with œstrone is only slight for males and doubtful for females. The ratio of the % increase in wt. of the prostate to that of seminal vesicles after injection of (I) is similar to that of gonadotropic hormone, but different from that observed during normal development. J. N. A.

Biological determination of the male hormone in carp. A. Beaune (Bull. Sci. pharmacol., 1935, 42, 193—199; Chem. Zentr., 1935, ii, 2835). R. N. C.

Treatment of inefficiency phenomena with male hormone. E. Braun (Deut. med. Woch., 1935, 61, 1482). R. N. C.

Protective action of progesterone on the genital organs of male mice. H. Burrows (Nature, 1936, 138, 164).—Progesterone protects the genital organs of non-castrated mice from the injurious effects of excessive dosage with œstrone. L. S. T.

Sexual hormones and related substances. IX. Substance having powerful action on the vesicular glands of the castrated male mouse. W. Dirscherl, J. Kraus, and H. E. Voss (Z. physiol. Chem., 1936, 241, 1—10; cf. this vol., 472).—Cryst. follicular hormone from mares' urine (and also probably stallions' but not men's urine) contains a substance (I) which on treatment with PtO_2+H_2 gives a hormone (II) having a powerful stimulating action on the vesicular glands of the castrated male mouse. The purest samples of (II) contained 1 mouse unit in 0·02 mg. and had no effect on the capon's comb. (II) (1 unit in 0·1—0·2 mg.) was also obtained without hydrogenation from wool fat and quassia bark. Other sex hormones also [*e.g.*, equilin, equilenin, testosterone (III)] probably contain (I) and/or (II). The conversion of (I) into (II) possibly involves conversion of :CO into :CH·OH and when this change is made in (III) the effect on the glands is increased tenfold. W. McC.

Action of follicular hormone on the thyroid of castrated women. M. Benazzi (Boll. Soc. ital. Biol. sperim., 1932, 7, 472—476). R. N. C.

Behaviour of calcium and potassium in the blood-serum of castrated bitches following treatment with follicular hormone. L. Manzi (Boll. Soc. ital. Biol. sperim., 1932, 7, 642—646).—Castration increases serum-K slightly without affecting Ca. Follicular hormone causes a rise of Ca, K remaining steady. R. N. C.

Primary hypercholesterolæmia in rabbits after administration of the luteinising hormone (prolan-*B*). G. Teilum (Compt. rend. Soc. Biol., 1936, 122, 981—984).—A few min. after injection, blood-cholesterol is increased by approx. 50%, returning to normal after approx. 1 hr. H. G. R.

Relation between excretion of chloride and that of water after injection of pituitrin. K. Unna and L. Walterskirchen (Arch. exp. Path. Pharm., 1936, 181, 681—688; cf. Dittmar, A., 1933, 1075).—In fasting dogs with fistulæ of the bladder subcutaneous and (at much lower concn.) intravenous injection of small doses of pituitrin (I) increases the urinary excretion of Cl′ without appreciably increasing the vol. of urine. The min. effective doses of (I) are the same as the min. doses required to inhibit diuresis in dogs receiving much H_2O and the excretion of Cl′ increases as the dose increases. Doses $\gg$ the min. effective increase the vol. of urine, the increase depending chiefly on the Cl′ excretion; small doses also increase the vol. in dogs on a diet rich in NaCl. W. McC.

Effect of extracts of anterior lobe of the pituitary on blood-sugar after elimination of the adrenals. K. J. Anselmino and F. Hoffmann (Arch. exp. Path. Pharm., 1936, 181, 674—680; cf. A., 1935, 1544).—In dogs with adrenals extirpated (or ligated) subcutaneous injection of extracts containing the pancreatropic hormone (I) produces great decrease in the blood-sugar. In the intact dog the increase is very slight because the increased secretion of insulin caused by (I) is followed by increased adrenaline output. After destruction of (I) by heat the action of the substance in the extracts which increases the blood-sugar is unaffected by removal or ligation of the adrenals. W. McC.

Effect of the fat-metabolism hormone of the anterior pituitary on ketone excretion by rats under experimental conditions. C. Sievert (Z. ges. exp. Med., 1935, 96, 429—441; Chem. Zentr., 1935, ii, 3255).—Spontaneous ketonuria under the conditions of Butts, Cuttler and Deuel, Burn, or Ging is caused by fasting or administration of a pure fat diet. The fat-metabolism hormone increases ketonuria on the fat diet, but not in fasting. The hormone in the blood after overcharging with fat corresponds with the pituitary hormone in its properties. R. N. C.

Pituitary hormones in cerebrospinal fluid. V. Colombi and V. Porta (Boll. Soc. ital. Biol. sperim., 1932, 7, 1103—1105).—The cerebrospinal

fluid of normal men and pregnant women contains no gonadotropic hormones, but exerts a slight oxytocic effect on the isolated uterus of the guinea-pig, even if the animal has been hypophysectomised. The fluid causes a slight increase of blood-pressure in dogs.
R. N. C.

Secretion of an antidiuretic pituitary hormone in response to the need for renal water conservation. A. Gilman and L. S. Goodman (Science, 1936, **84**, 24—25).—The posterior pituitary of rats and dogs secretes an antidiuretic hormone which acts on the kidney, escaping ultimately into the urine, in which it is relatively stable. The need for H_2O conservation by the body is the stimulus for secretion.
L. S. T.

Biological effects of homologous thymus implants in successive generations of rats. N. H. Einhorn and L. G. Rowntree (Science, 1936, **84**, 23—24).—Frequent implants in albino rats accelerate the rate of growth and development of the young, similarly to daily injections of thymus extract.
L. S. T.

Effect of various hormones on the blood picture, especially on nuclear displacement according to Arneth. I. Thyroid gland. II. Effect of insulin in the correlation between thyroid and insulin. S. Morimoto (Folia Endocrinol. Japon., 1934, **9**, 105—106).—I. After feeding thyroid and in Basedow's disease the blood picture shows a " left shift," and after thyroidectomy a right shift. Thyroid hormone probably stimulates leucopoiesis in bone-marrow.

II. Injection of insulin into rabbits causes a right shift followed by a left shift in the blood picture. Leucocyte changes involved are arrested by feeding thyroid. In thyroidectomised animals leucocyte changes are slow. Ch. Abs. (*p*)

Effect of the blood-serum of rabbits, in which the thyroid function has been experimentally disturbed, on tissue respiration. K. Mune (Folia Endocrinol. Japon., 1934, **9**, 102—103).—The O_2 consumption of rat muscle is > normal when suspended in serum of hyperthyroidised rabbits, and < normal when in serum of thyroidectomised rabbits.
Ch. Abs. (*p*)

Association and dissociation reactions of thyroglobulin. H. P. Lundgren (Nature, 1936, **138**, 122).—Previous work (A., 1935, 1522) has been confirmed. Conditions which favour dissociation are low concn. of thyroglobulin (I), low salt concn., high temp., ε, and p_H. Under appropriate conditions, (I) dissociates or associates at slow, measurable rates into components of lower or higher mol. wt. having well-defined sedimentation boundaries. These rates are too slow under the conditions existing in the living cell for these factors alone to account for the mechanism of (I) economy in the body. L. S. T.

Relations between parathyroid hormone and vitamin-*D*. M. Coppo and P. Frugoni (Boll. Soc. ital. Biol. sperim., 1934, **9**, 148—151).—Growth of rats is diminished by excess and prevented by absence of vitamin-*D*; parathormone (I) causes loss of wt. in both cases. The ash content of the body is diminished, but its Ca and P contents are increased and the Ca/P ratio is diminished in all cases, the increase and diminution being less if (I) is given. -*D* and (I) do not appear to exhibit antagonism in thyro-parathyroidectomised animals. R. N. C.

Effect of parathyroid hormone on serum-calcium and calcium excretion of normal and adrenalectomised rats. L. I. Pugsley and J. B. Collip (Biochem. J., 1936, **30**, 1274—1279).—A possible relationship between the adrenal and parathyroid glands is investigated. Adrenalectomised rats show a greater increase in serum- and urinary Ca following injection of parathyroid hormone (I) than do normal rats. With adequate Ca-containing diets, continued injection of (I) produces decreasing responses until the serum- and urinary Ca remain normal.
H. D.

Explanation of adrenaline action. W. J. R. Camp and J. A. Higgins (Science, 1936, **83**, 622).—Most of the changes effected by adrenaline are actually produced by K. L. S. T.

Effect of adrenal capsule on the regulation of blood-sugar. I. Effect of adrenalectomy. II. Effect of removal of the cortex and of the medulla of adrenal capsules. K. Yagi (Folia Endocrinol. Japon., 1934, **9**, 113—114, 114—115).—I. In adrenalectomised rabbits a single administration of sugar causes an increase in blood-sugar (I) > that produced in normal animals. The return to normal level is also accelerated. The Staub effect after two administrations of sugar was more marked in treated rabbits.

II. After cauterisation of the cortex of both adrenal capsules the Starke effect was decreased, the increase in (I) was greater, the duration of hyperglycæmia was longer, and the ability to assimilate carbohydrates < that of normal animals. Cauterisation of the medulla produced opposite effects. Ch. Abs. (*p*)

Effect of age and method of administration on adrenaline action. M. Hasegawa (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharm. Soc., 1933, 14—15). Ch. Abs. (*p*)

Adrenaline in the adrenal glands of dogs under low atmospheric pressures. L. Binet and J. Lanxade (Compt. rend. Soc. Biol., 1936, **122**, 1011—1012).—The val. is doubled in 1 hr. at pressures equiv. to an altitude of 10,000 m. H. G. R.

Biological assay of the adrenal cortical hormone by the survival of young [adrenalectomised] rats. P. Schultzer (Compt. rend. Soc. Biol., 1936, **122**, 978—981; cf. A., 1935, 1421).
H. G. R.

Action of thyroid hormone on cells grown *in vitro*. J. Verne and D. Odiette (Compt. rend. Soc. Biol., 1936, **122**, 988—990).—Plasma after injections of thyroxine at first augments and, after repeated injections, retards the growth of *in-vitro* cultures of fibroblasts of chick embryo. H. G. R.

Isolation of a hypoglycæmic principle in the jejunal mucosa. F. Rathery, A. Choay, and P. de Traverse (Compt. rend., 1936, **202**, 1949—1950).—An aq. EtOH extract of the jejunal mucosa of the ox contains a substance, 10—20 mg. of which lowers the blood-sugar of a rabbit and may produce convulsions. J. L. D.

Standardisation of insulin. J. Štefl (Arch. exp. Path. Pharm., 1936, **181**, 617—624).—The method is based on determination of the amount of the material containing insulin required to produce hypoglycæmic convulsions in rabbits. Abs. specificity is attained by taking account only of convulsions which are arrested by injection of glucose. The average experimental error is ±20%. W. McC.

Changes in the glutathione content of the blood after insulin treatment. L. Liaci (Biochim. Terap. sperim., 1933, **20**, 329—332; Chem. Zentr., 1935, ii, 2837).—Blood-glutathione is increased. R. N. C.

Action of insulin in pregnancy. E. Sapegno (Boll. Soc. ital. Biol. sperim., 1932, **7**, 690—691).—The action of insulin in pregnant rabbits is the same as in normal animals, but the effect of the hypoglycæmia on body-temp. is more marked. R. N. C.

Insulin and experimental beri-beri in the pigeon. A. Baglioni and V. Console (Boll. Soc. ital. Biol. sperim., 1934, **9**, 153—155).—Insulin (I) lowers the beri-beri quotient in vitamin-*B*-deficient pigeons to an extent ∝ the quantity of (I) injected, and retards the appearance of the beri-beri symptoms. The effect is not due to anti-beri-beri action of (I), which appears to antagonise -*B*. R. N. C.

Absorption spectra as an aid to vitamin research. H. Rudy (Naturwiss., 1936, **24**, 499—505).—A review.

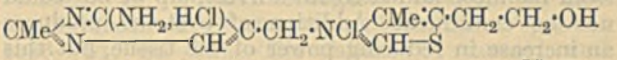
Photochemical decomposition of vitamin-*A* in alcoholic solution. I. Primary reactions. A. Chevallier and P. Dubouloz (Bull. Soc. Chim. biol., 1936, **18**, 703—722).—Vitamin-*A* in slightly acid EtOH solution is decomposed by light of λ 3650 A. giving two substances in const. proportion characterised by their absorption spectra and solubility, the quantum yield being 1/28. From the kinetics of the decomp. a method for the determination of -*A* in blood is proposed. Irradiation of -*A* in alkaline EtOH solution does not cause the same decomp. A. L.

Primary, secondary, and non-specific effects of experimental *A*-avitaminosis in rats. T. H. de Ruyter and O. Rosenthal (Z. Vitaminforsch., 1936, **5**, 169—185).—Primary effects include atrophy and metaplasia of epithelial tissue and atrophy of the lymphatic system, secondary are cessation of growth, loss of appetite, and susceptibility and lowered resistance to infection, whilst indirectly secondary are anæmia and changes in fat metabolism. F. O. H.

Action of vitamin-containing ointments on the healing of wounds. H. J. Lauber and H. Rocholl (Klin. Woch., 1935, **14**, 1143—1146).—Vitamin-*A* added to cholesterol ointments accelerates the healing effect in small and medium doses, but slightly restrains it in large doses. R. N. C.

Determination of vitamin-*A*. J. F. Ward and R. T. M. Haines (Nature, 1936, **138**, 128; cf. this vol. 646). L. S. T.

Structure of vitamin-B_1. R. R. Williams (J. Amer. Chem. Soc., 1936, **58**, 1063—1064).—Cleavage of vitamin-B_1 (I) with liquid NH_3 gives a base, $C_6H_{10}N_4$, the absorption of which resembles that of a 6-amino-5-alkylpyrimidine. The aminosulphonic acid (A., 1935, 1035) and Na in liquid NH_3 afford a little 6-amino-2 : 5-dimethylpyrimidine. The hydroxysulphonic acid (*loc. cit.*) is 6-hydroxy-2-methyl-5-sulphomethylpyrimidine. The compound, $C_7H_{11}O_5N_3$, of Windaus *et al.* (A., 1934, 1415) is probably 6-hydroxy-5-ethoxymethylpyrimidine nitrate. The following structure is now assigned (cf. A., 1935, 504) to (I).



H. B.

Rôle of adenylic acid in vitamin-B_1 deficiency. T. W. Birch and L. W. Mapson (Nature, 1936, **138**, 27—28).—Adenosine, or adenylic acid (I) from muscle or yeast, increases the bradycardia present in rats deficient in vitamin-B_1. The -B_1-deficient animals are unable to render these compounds innocuous at the same rate as does the normal animal. The deaminase activity of -B_1-deficient cardiac tissue is 20% < that of similar tissues on full diet. This failure of the deaminase mechanism may result in increased accumulation of (I) in the tissue, which is the cause of bradycardia. Other effects, *e.g.*, increased lactic acid and decreased O_2 consumption, obtained with -B_1-deficient tissue may be due to the inhibition by (I) of oxidative mechanisms which are responsible for the removal of these metabolites. L. S. T.

Determination of reduced ascorbic acid in blood-serum and plasma. F. H. L. Taylor, D. Chase, and J. M. Faulkner (Biochem. J., 1936, **30**, 1119—1125).—Reduced ascorbic acid (I) is determined in 2 c.c. of serum or plasma by pptg. the proteins with tungstic acid and titrating the filtrate with 2 : 6-dichlorophenol-indophenol. For accuracy it is necessary to dissolve and reppt. the proteins several times. In 33 normal human sera, (I) varied from 0·83 to 2·43 (average 1·61), whilst in 10 scorbutics, the max. val. was 0·55 mg. per 100 c.c. W. O. K.

Determination of ascorbic acid. A. Emmerie and M. van Eekelen (Z. physiol. Chem., 1936, **241**, 134).—Wachholder *et al.* (this vol., 766) have overlooked the procedure of the authors (*ibid.*, 255). W. McC.

Determination of vitamin-*C* by Bezssonoff's method. N. Bezssonoff and E. Stoerr (Z. Vitaminforsch., 1936, **5**, 193—221).—The technique of the use of monomolybdophosphotungstic acid in determining vitamin-*C* in urine, blood, cerebrospinal fluid, milk, adrenal gland, liver, and vegetable tissues is described (cf. A., 1935, 670). F. O. H.

Vitamin-*C* content of the ocular fluids and tissues with particular reference to the aqueous humour and the crystalline lens. G. Bietti and A. Cartenì (Boll. Soc. ital. Biol. sperim., 1934, **9**, 283—286).—Analytical vals. are given for the aq. humour and cryst. lens of the ox, sheep, rabbit, and dog. Ascorbic acid is present in other ocular tissues. The content depends on age and the nutritional state. R. N. C.

Variations in the ascorbic acid content of the ovaries, particularly in the corpus luteum. A.

Giroud, I. Cesa, R. Ratsimamanga, and M. Rabinowicz (Compt. rend. Soc. Biol., 1936, **122**, 899—901).—Ascorbic acid in the corpus luteum increases during the period of formation and decreases during degeneration. H. G. R.

Alleged formation of vitamin-*C* from mannose by liver-pulp. R. Ammon and G. Grave (Z. Vitaminforsch., 1936, 5, 185—192).—The claim of Guha and Ghosh (A., 1935, 131) that vitamin-*C* is formed from mannose added to rat's liver-pulp at 38° could not be confirmed. Addition of cysteine produces an increase in reducing power of the tissue, but this is probably due to the experimental method. F. O. H.

Relations between ascorbic acid and glutathione. F. G. Hopkins and E. J. Morgan (Biochem. J., 1936, **30**, 1446—1462).—The velocity of oxidation of ascorbic acid (I) by hexoxidase (II) $\propto$ concn. of (II), varies with p_H, and is const. with time. Glutathione (III) alone is unaffected by (II) but inhibits the oxidation of (I) by (II), being oxidised itself at the same rate as (I) when alone; when (III) is almost completely oxidised the oxidation of (I) begins. 0·002*M*-KCN inhibits the oxidation. The rate of oxidation of (I) is 1/5 that of reduction of the oxidised (I) anaërobically induced by adding (III) when the oxidation is complete. When a dialysed prep. of (II) is used the rate of reduction diminishes rapidly with time. At p_H 7·4 (I) is rapidly autoxidised in the presence of Cu, and (III) much more slowly; when both (I) and (III) are in solution together (I) is wholly protected from oxidation although the oxidation of (III) is unchanged. At p_H 6·0 neither constituent of the mixture is oxidised. Suspensions of liver-tissue from well-fed rabbits show an intial reduction of (III) followed by oxidation whilst the concn. of (I) remains approx. const. With liver from animals starved for 48 hr. oxidation of both (III) and (I) occurs immediately and rapidly; addition of a large excess of (III) inhibits the oxidation of (I). H. D.

Ascorbic acid and glutathione contents of immunised animals. H. I. Jusatz, T. Bersin, and H. Köster (Klin. Woch., 1935, **14**, 1419—1420).—Blood-glutathione (I) in rabbits is depressed by immunisation with horse serum. Both (I) and ascorbic acid (II) are lowered in the adrenals of immunised animals fed on a diet poor in vitamin-*C*. (I) and (II) are utilised in antibody formation during immunisation. R. N. C.

Destruction of ascorbic acid in water. H. C. Hou (J. Chinese Chem. Soc., 1936, 4, 224—234).—Ordinary distilled H_2O and Shanghai tap-H_2O have a marked destructive effect on ascorbic acid (I). This effect is considerably reduced when the solutions are sterilised, and hence is at least partly due to certain micro-organisms, the addition of which increases the destructive effect of a sterilised solution. Certain other organisms have a stabilising effect. Aq. (I) is only slightly decomposed when heated rapidly to the b.p. F. R. S.

Reduction of iron by tissue extracts and by ascorbic acid, with a note on the stabilisation of ascorbic acid solutions. W. D. McFarlane (Biochem. J., 1936, **30**, 1472—1478).—Reduction of tissue-Fe *in vivo* by ascorbic acid (I) involves some form of Fe-protein complex. Catalytic oxidation of (I) by Cu is inhibited by Na diethyldithiocarbamate (II), cystine, cysteine, and glutathione, and the aërobic oxidation in orange juice by 2 : 2′-dipyridyl (III) and (II) together; this is not affected by (II) alone and may be increased by (III). H. G. R.

Reversible oxidation of ascorbic acid demonstrated by assays with guinea pigs. N. Bezssonoff and M. Woloszyn (Compt. rend. Soc. Biol., 1936, **122**, 944—946).—Biological tests confirm the modification of the properties of vitamin-*C* in biological media as compared with those in pure solution (cf. this vol., 255). H. G. R.

Oxidation of vitamin-*C*. N. Bezssonoff and M. Woloszyn (Compt. rend. Soc. Biol., 1936, **122**, 941—944).—It is suggested that a hypothetical "diascorbic ether" is an intermediate in the oxidation of ascorbic to dehydroascorbic acid. H. G. R.

Effect of light on production and distribution of ascorbic acid in germinated soya-beans. W. Y. Lee and B. E. Read (J. Chinese Chem. Soc., 1936, 4, 208—218).—Soya beans germinated at 25° in the dark form ascorbic acid (I) in increasing amount up to the 9th—11th day when approx. 0·4 mg. per seedling is present largely in the reversibly oxidised form. Sunlight increases production of (I), and the possible correlation of these results with the development of the plant and the formation of chlorophyll is discussed. F. R. S.

Formation and distribution of vitamin-*C* in the germinating pea, *Pisum sativum*, L. W. Y. Lee (J. Chinese Chem. Soc., 1936, 4, 219—223).—Peas sprouted in the dark for 13 days have a max. content (0·040%) of ascorbic acid on the 8th day. The vitamin is apparently formed in the cotyledons, which have a relatively high content by the 6th day. F. R. S.

Rôle of vitamin-*C* in animals resistant to scurvy: effects of insulin and adrenaline. K. M. Daoud and M. A. S. el Ayyadi (Biochem. J., 1936, **30**, 1280—1292).—The rate of urinary excretion of vitamin-*C* by rats is decreased by a scorbutic diet or injection of adrenaline (I), and increased by 24 hr. starvation. The -*C* content of the adrenals is not affected by a scorbutic diet, 24 hr. starvation, or injection of insulin (II) or (I), whilst that of the liver is increased by injection of (II) in rats on a scorbutic diet but not by (I). The quantity of -*C* in the bodies of rats influences the glycogenolytic response to (I). H. D.

Vitamin-*C* requirements of the guinea-pig. S. S. Zilva (Biochem. J., 1936, **30**, 1419—1429).—The relationship of the intake of ascorbic acid (I) to the content in the tissues, the susceptibility to scurvy, and the urinary excretion of (I) is investigated. With scorbutic guinea-pigs (I) appeared in the tissues after injection of 5—8 mg. per day and reached a limiting concn. when 20 mg. per day were injected; increasing the dose caused excretion of (I) in the urine. The time taken for a guinea-pig to die on a scorbutic diet was independent of the amount of (I) previously ingested. H. D.

Allergy and vitamin-*C*. A. Hochwald (Zentr. inn. Med., 1935, **56**, 769—771; Chem. Zentr., 1935, ii, 2692).—Vitamin-*C* and glutathione inhibit anaphylactic but not histamine shock. R. N. C.

Behaviour of vitamin-*C* in Addison's disease. S. Siwe (Klin. Woch., 1935, **14**, 1311—1313).—Vitamin storage is not increased by excessive dosage, the excess being excreted immediately in the urine. R. N. C.

Capillary resistance. IV. Effect of vitamin-*C* therapy on lowered capillary resistance in patients with gastric achylia. P. Schultzer and O. Griis (Acta med. scand., 1935, **85**, 563—573).—Normal resistance is re-established in certain cases. R. N. C.

Cataract and ascorbic acid in the guinea-pig eye. S. W. Johnson (Biochem. J., 1936, **30**, 1430—1437).—The ascorbic acid (I) content of the aqueous humour and lens, determined both by titration and spectrographically, became zero after 9 days on a scorbutic diet; the rate of disappearance and reappearance after injection ran parallel with that in other tissues. No cataract appeared in animals devoid of (I). H. D.

Vitamin-*D* in child health. F. O. Tonney (Amer. J. Publ. Health, 1936, **26**, 665—671).—A review.

Formation of a sulphate salt of the antirachitic vitamin. A. E. Sobel, G. Goldstein, and B. Kramer (J. Amer. Chem. Soc., 1936, **58**, 1056—1057).—Calciferol (I) and C_5H_5N,SO_3 in C_5H_5N–C_6H_6 give C_5H_5N calciferyl sulphate which, unlike the ergosteryl and cholesteryl salts (A., 1935, 903), is hydrolysed by aq. KOH to (I). Approx. 60% of the vitamin-*D* (II) present in cod-liver oil concentrates is separable by successive treatment with C_5H_5N,SO_3 and aq. KOH in presence of light petroleum [which dissolves (II)]. H. B.

Energy equivalents of vitamin-*D* units. R. W. Haman and H. Steenbock (Ind. Eng. Chem. [Anal.], 1936, **8**, 291—293).—Measurements of the energy absorbed when ergosterol is converted into vitamin-*D* shows that an international unit requires 900 ergs and a Steenbock unit 3000 ergs. Biological tests for potency give a similar ratio. S. C.

Mode of action of vitamin-*D*. I. Phosphorus compounds in muscles, liver, and kidneys as influenced by different levels of vitamin-*D* and phosphorus in the diet. R. Nicolaysen (Biochem. J., 1936, **30**, 1329—1337).—In rachitic rats, the vals. for inorg. P+phosphagen of muscle and for inorg. P of liver and kidneys are < for rats on the same diet, but with addition of therapeutic amounts of vitamin-*D*. A similar reduction was obtained in lipin-P and protein-P in liver and kidneys of rachitic rats but not in muscle. No definite change was observed in readily or difficultly hydrolysable esters in muscles or liver or the difficultly hydrolysable esters of kidney. When P was added to the rachitic diet and the Ca content reduced, the animals remained normal and gave the same results as on the rachitic diet+-*D*. Addition of -*D* to this P-richer diet, although giving better calcified bones, did not influence the amounts of P compounds in muscle, liver, and kidney. Massive doses of -*D* administered for short periods to rachitic rats increased inorg. P to the normal level in muscle, liver, and kidneys and for 2 weeks resulted only in an increase of inorg. P in the kidneys up to double the normal val. P. W. C.

Isomerides of cholesterol and experimental rickets. II. Pharmacological action of *iso*cholesterol. U. Sammartino (Arch. Farm. sperim., 1936, **61**, 88—96).—The failure of normal and irradiated *iso*cholesterol to replace totally vitamin-*D* in the cure of rats on a rachitogenic diet is similar to that of *allo*- or β-cholesterol (cf. A., 1933, 1088). F. O. H.

Cereals and rickets. VII. Rôle of inorganic phosphorus in calcification on cereal diets. J. T. Lowe and H. Steenbock (Biochem. J., 1936, **30**, 1126—1134).—Autolysed, germinated, immature, and HCl-treated maize are less rachitogenic than is mature maize due to the higher content of inorg P. The inorg. P content of variously treated samples of maize varied directly with their antirachitic action and inversely with their phytin (I) content. (I) fed to rats was a poorly available source of P as compared with inorg. P or Na glycerophosphate (cf. A., 1934, 682). As acid-treated maize produced slightly better calcification than could be accounted for by its inorg. P content, it is possible that other factors still undiscovered play a part in rickets. W. O. K.

Antirachitic action of the irradiated unsaponifiable fraction of lanoline. M. de Caro (Boll. Soc. ital. Biol. sperim., 1932, **7**, 1097—1099; Chem. Zentr., 1935, ii, 2839).—Experiments with rats point to a definite antirachitic activity. H. N. R.

Effect of cod- and tunny-liver oils and of irradiated ergosterol and cholesterol preparations on avian rickets. M. J. L. Dols (Z. Vitaminforsch., 1936, **5**, 161—169).—Equiv. amounts (as measured in rat-units) of the oils or irradiated cholesterol preps. are effective in healing avian rickets, whilst 10 times this dosage of irradiated ergosterol is insufficient. Calciferol is therefore not identical with the vitamin-*D* in fish-liver oils, whilst the provitamin-*D* of impure cholesterol is not ergosterol. F. O. H.

Antirachitic vitamin from tunny-liver oil. H. Brockmann (Z. physiol. Chem., 1936, **241**, 104—115).—The oil on treatment with light petroleum and MeOH followed by chromatographic adsorption on Al_2O_3 using a red indicator, production of a crude 3 : 5-dinitrobenzoate, and repetition of the adsorption yields vitamin-D_3, $[\alpha]^{17}_D$ +100° in $CHCl_3$, identical with the irradiation product of 7-dehydrocholesterol. -D_3 combines with maleic anhydride. W. McC.

Antirachitic substance from tunny-liver oil. G. A. D. Haslewood and J. C. Drummond (Chem. and Ind., 1936, 598—599).—Tunny-liver oil, containing no vitamin-*A* and 80,000 international units (I.U.) per g. of -*D*, gave an inactive fraction, selective absorption at 2760 A., and a strongly adsorbed fraction with antirachitic activity of $1{\cdot}5\times10^6$ I.U.

A specimen of oil, containing -*A*, 90,000 I.U. and -*D*, 30,000 I.U., has been converted into a mixture of allophanates, the most insol. portion having m.p. 185—195°, hydrolysed to a fraction of activity $10-20\times10^6$ I.U. The substance obtained by Brockmann (preceding abstract) is probably not identical with that now described. F. R. S.

Antirachitic activity for chicken and rat of vitamin-*D* from various sources. A. Black and H. L. Sassaman (Amer. J. Pharm., 1936, **108**, 237—243).—Blue fin, yellow fin, and striped tuna-liver oils contain a vitamin half as active for chicken as for rat. Oils from swordfish, halibut, mackerel, cod, and irradiated cholesterol show no difference, whilst irradiated phytosterol and unsaponifiable matter from lucerne simulate irradiated ergosterol. E. D. Y.

Determination of vitamin-*D*. H. Brockmann and Y. H. Chen (Z. physiol. Chem., 1936, **241**, 129—133).—Vitamin-D_2 and -D_3 are colorimetrically determined even in presence of a 5—6-fold excess of -*A* by means of the orange colour reaction with $SbCl_3$ in $CHCl_3$. Vegetable oils and other sterols (except tachysterol) and sterol derivatives do not interfere unless present in very large excess. EtOH must be absent. W. McC.

Constituents of rice embryo. II. Vitamin-*E*. R. H. Kimm (J. Agric. Chem. Soc. Japan, 1935, **11**, 514—523).—The unsaponifiable matter, after removal of sterols, yields on distillation an oil containing vitamin-*E* and a hydrocarbon, $C_{15}H_{16}$, devoid of -*E* activity. Ch. Abs. (*p*)

Vitamin-*P*. Flavanols as vitamins. S. Rusznyák and A. Szent-Györgyi (Nature, 1936, **138**, 27).—*Vitamin*-P, closely allied to -*C*, cures pathological fragility and permeability of the capillary walls to plasma protein. It occurs in Hungarian red pepper and lemon juice, and appears to be flavone or flavonol glucoside. L. S. T.

Respiration of mango leaves (*Mangifera indica*). N. K. Chatterji (Proc. Nat. Acad. Sci. India, 1936, **6**, 149—160).—The CO_2/O_2 relationship of young (red), mature (green), and old (yellow) leaves is examined. The O_2 intake exceeds the CO_2 output in red and green but not in yellow leaves. The apparently excessive O_2 intake is partly utilised during the conversion of sugars into org. acids in the leaves. In yellow leaves the low O_2 intake is attributed to actual liberation of O_2 resulting from the production of fats from sugars. A. G. P.

Anaërobiosis in higher plants. K. Paech (Planta, 1935, **24**, 529—551).—After short anaërobiosis and prior to the onset of irreversible injury, changes occur in the η and permeability of the protoplast similar to those characteristic of narcosis. There is no evidence that the changes result from the formation of an anaërobic product in the system. The $EtOH/CO_2$ ratio in the products of anaërobic metabolism is much nearer to theoretical val. than is usually supposed. Instances of an apparently large excess of CO_2 produced are attributed to faulty analysis. Cases of smaller excess may be due to further oxidation of a portion of the EtOH by H-acceptors present in the cell. Anaërobic metabolism is similar to alcoholic fermentation. A. G. P.

Effects of soil drought on photosynthesis and respiration in plants. A. A. Zaitzeva (Bull. Acad. Sci. U.R.S.S. [Sci. math. nat.], 1935, 19—39).—Respiration of wheat plants was reduced during wilting and remained below normal 40—48 hr. after watering. Increased photosynthesis was observed 20—40 hr. after watering. Ch. Abs. (*p*)

Tropical fruits. I. Development, ripening, and senescence with special reference to respiration. C. W. Wardlaw and E. R. Leonard. **II. Internal gas concentrations in fruit.** C. W. Wardlaw (Ann. Bot., 1936, **50**, 621—653, 655—676).—I. Changes in the $[O_2]$ and $[CO_2]$ in the interior of large hollow fruits (*e.g.*, papaw) are examined. An increase in $[CO_2]$ appears prior to the onset of the climacteric and continues steadily thereafter, without any sp. change corresponding with the peak vals. seen in "external" respiration. The post-climacteric decline in external respiration corresponds with a decrease in internal $[O_2]$ which continues until anaërobic conditions are reached. The onset of ripening is associated with a peak val. for $[O_2]$. The later, senescent, stage probably results from failure of O_2 to gain access to fleshy tissue.

II. Changes in internal gas concn. resulting from modification of the external atm. are examined. The rate of respiration as determined by evolution of CO_2 from the external surface is not necessarily a reflexion of cellular respiration and is influenced by the CO_2 present in the flesh. High initial rates on removal of fruit from air to N_2 are due to adjustment between internal and external $[CO_2]$. Subsequent metabolism proceeds at < normal rates. A. G. P.

Assimilation and respiration of tropical trees of West Java. O. Stocker (Planta, 1935, **24**, 402—445).—Effects of temp. and light intensity are examined. The quotient, max. assimilation ÷ respiration indicates that dry matter production and H_2O exchange in plants in all climates fall within certain limits. Variations among species in the same habitat are > the average variation from habitat to habitat. A. G. P.

Do cut leaves give physiologically correct assimilation values? P. Bauer (Planta, 1935, **24**, 446—453).—Assimilation in cut leaves examined for short periods ($\not> 1$ hr.) is the same as that in intact leaves. A. G. P.

Transport in the cotton plant. V. Oxygen supply and the activation of diffusion. T. G. Mason and E. Phillis (Ann. Bot., 1936, **50**, 455—499; cf. this vol., 531).—Coating leaf petioles with wax caused an increase and subsequent decline in the carbohydrate (I) content of the lamina and increased the (I) and P in the petiole. Exclusion of O_2 from stems may restrict transport through them but the restriction of growth is much more marked. When the O_2 supply through lenticels is cut off some O_2 may be obtained from the transpiration current. Coating defoliated stems checked the movement of (I) and N to similar extents and that of P, K, and Mg to a smaller degree. Activation of diffusion probably depends on a special organisation in the cytoplasm, maintained by metabolic energy, which lowers the resistance to solute movement sufficiently to permit diffusion in the sieve tube at rates comparable with those in a gas. A. G. P.

Effect of potassium on the nitrogen economy of etiolated and green seedlings. H. Jaenichen (Angew. Bot., 1935, **17**, 374—445).—The growth and succulence of rape, wheat, and maize seedlings increases with the K supply to a max. beyond which larger applications of K have the reverse effects. In amounts $\not>$ optimum K increases the intake and storage of H_2O, and the influence of K on the nutrient intake and N distribution of the plants is largely attributable to the improved H_2O status of the tissues. Differences in the interpretation of analytical data expressed as % of fresh wt. and as total per leaf or plant are emphasised. A. G. P.

Radio-physiological importance of potassium in chlorophyll-containing and -free cells. J. Stoklasa (Strahlenther., 1935, **53**, 276—295; Chem. Zentr., 1935, ii, 2833—2834).—β- and γ-Rays emitted by K accelerate germination, and increase dry matter yield, by their action on the photosynthetic process. Photosynthetic assimilation of CO_2 occurs only in the presence of K and for this purpose Mg cannot replace K. A. G. P.

Seasonal variations in *Chondrus crispus*. M. R. Butler (Biochem. J., 1936, **30**, 1338—1344).—The ash, N, and carbohydrate contents of a series of monthly collections of this marine alga from the same locality are compared with the corresponding contents of the polysaccharide complex (I) extracted therefrom by the method already described (A., 1934, 1047). Similar variations occur in the ash contents of both the whole plant and of (I). The N present in (I) depends directly on the N content of the plants. The carbohydrate content (%) is low until March or April, then increases, and a high level extends from May to October. Carbohydrate and SO_4'' determinations show that an acid type of ester predominates from January to May, the normal type from May to October, whilst from October to January there appears to be a gradual return to the acid type of salt. P. W. C.

Supply of iron to cultivated plants. P. Ehrenberg (Z. Pflanz. Düng., 1936, **45**, A, 1—55).—The causes of Fe chlorosis, and soil conditions influencing the availability of Fe, are reviewed. An extensive bibliography is given. A. G. P.

Effect of aluminium ions on plant growth. K. Scharrer and W. Schropp (Z. Pflanz. Düng., 1936, **45**, A, 83—95).—Toxicity tests with various $[Al^{\cdot\cdot\cdot}]$ in sand and H_2O cultures are recorded. The sensitivity of various crops was in the descending order, barley, wheat, rye, oats, maize, *i.e.*, almost the same order as the susceptibility to $H^{\cdot}$. In some instances small $[Al^{\cdot\cdot\cdot}]$ increased the yield of oats and maize. Al caused root injury in all cases. A. G. P.

Dependence of the [plant] "condition indicators" on salt nutrition. Wheat. W. H. Fuchs (Planta, 1935, **24**, 725—741; cf. A., 1935, 904).—The influence of $Na^{\cdot}$, $K^{\cdot}$, $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, Cl', SO_4'', and NO_3' in nutrient media on the osmotic pressure, conductivity, and sugar level of the expressed sap of wheat seedlings is examined. A. G. P.

Nutrient supply and water requirements in cereals and pasture plants. A. H. K. Petrie (J. Austral. Inst. Agric. Sci., 1935, **1**, 77—78).—Increased N supply has no effect on the transpiration rate per unit wt. of leaf but increases the ratio of leaf to whole plant throughout most of the growing period. Reduction in transpiration ratio following increased N supply is effected by the action of N on growth. Increasing P supply lowers the transpiration per unit wt. of leaf and the leaf : total wt. ratio. The resulting decrease in respiration per unit wt. of plant is $>$ the increase produced by the growth effect of P. Ch. Abs. (*p*)

Hydrogen-ion concentration and titratable acidity at different stages of fruit ripening. N. L. Pal (Proc. Nat. Acad. Sci. India, 1936, **6**, 131—135).—Data for *Lycopersicum esculentum*, *Psidium guayava*, *Citrus medica*, and *C. aurantium* at different stages of maturity are given. The $[H^{\cdot}]$ increased over the greater part of the period but declined in the final stages. The titratable acidity increased steadily throughout except in the case of *Lycopersicum*. No direct relationship was apparent between the two sets of vals. A. G. P.

Plant growth-substances. XIX. Effect of unknown factors on the response of *Avena sativa*. F. Kögl, A. J. Haagen-Smit, and C. J. van Hulssen (Z. physiol. Chem., 1936, **241**, 17—33; cf. this vol., 122).—The great variations in the sensitivity of plants to auxins are not due to changes in atm. pressure, intensity of cosmic rays, electrical state of the atm., or p.d. in the plant. The unknown factors which cause the variations appear to be responsible for parallel variations in the respiration and movement of the protoplasm, whilst the nature of the illumination (red or orange light) has a definite effect. W. McC.

Electrotropism in pollen tubes. H. D. Wulff (Planta, 1935, **24**, 602—608).—Growth of pollen tubes through the tissue of the style is probably related to the movement of growth-substance in the tube under the influence of the potential gradient in the style. A. G. P.

Plant tissue cultures from a hormone viewpoint. J. Bonner (Proc. Nat. Acad. Sci., 1936, **22**, 426—430).—Means of purification of plant hormone-containing materials and of examining their potency in bean tissue cultures are described. A. G. P.

Endosperm growth-substance and the growth-substance of the coleoptile tip. R. Pohl (Planta, 1935, **24**, 523—526).—The growth of the oat coleoptile in light and in darkness is controlled by the growth-substance (I) in the endosperm. The tip does not produce (I) but activates the reserve from the endosperm. The shorter growth of the coleoptile in light may be due to the lower activity of (I), or to smaller ability of the cells to react to (I) in daylight than in darkness. The ability of cells to stretch is not lessened in light, since they respond equally in light and darkness to (I) from urine or to β-indolylacetic acid paste. A. G. P.

Influence of β-indolylacetic acid on leaf movement and the formation of adventitious roots in *Coleus*. O. Fishnich (Planta, 1935, **24**, 552—583).—Application of β-indolylacetic acid to stems induces root initiation only from treated areas. With leaf stems and midribs response is slower and roots appear on the underside of the leaf at a distance from the point of application and later on the stem at a distance of 2—3 nodes. A. G. P.

Light-growth response and auxin curvatures of *Avena*. J. van Overbeek (Proc. Nat. Acad. Sci., 1936, **22**, 421—425).—The rate of curvature of decapitated coleoptiles treated unilaterally with auxin-*A* shows a similar response to continuous exposure to light as does the growth rate of the intact seedling on illumination (base growth response). The initial light-growth response of the *Avena* coleoptile (decrease in growth rate) is comparable to the response of the *Raphanus* hypocotl. A. G. P.

Plant growth effects of heteroauxin applied to soil and plants. W. F. Loehwing and L. C. Bauguess (Science, 1936, **84**, 46—47).—Addition of a dil. solution of β-indolylacetic acid (I) to the soil produces a transitory acceleration of growth in stock seedlings. Symptoms due to accelerated growth also appear when localised areas of the plants are treated with (I). L. S. T.

Vitamins and growth factors in plants. Solubility of growth factors. The factor in urine. W. H. Schopfer (Arch. Mikrobiol., 1935, **6**, 290—308).—Small amounts of a growth-substance affecting *Phycomyces* are obtained from wheat germ by extraction with $CHCl_3$ and from rice polishings with C_6H_6. The solubility of the active materials and of the growth factor from urine is compared and the possible identity of these factors with vitamin-B_1 is discussed. A. G. P.

Presence of free sugar in green algæ and its relation to photosynthesis. I. *Codium latum*, Suringar. II. *Cladophora Wrightiana*, Harvey. S. Endo (Sci. Rep. Tokyo Bunrika Daigaku, 1936, **2**, B, 223—231, 291—295).—I. Glucose (I), non-reducing polysaccharide (II) of low mol. wt., and starch (III) are present. The variations in their levels from day to day and with difference in intensity of light indicate that (I) is the first product of photosynthesis of carbohydrate.

II. Fructose (the first product of photosynthesis) and (II), but not (III), are present. F. O. H.

Plant nutrition. V. Carbohydrate metabolism in relation to nutrient deficiency and to age in barley leaves. F. G. Gregory and E. C. D. Baptiste (Ann. Bot., 1936, **50**, 579—619; cf. this vol., 908).—In sand-cultured barley N deficiency increased the total sugar (I) content but had no consistent effect on the reducing sugars (II) of fully emerged leaves. P deficiency increased (II) but had a much smaller effect on (I). K deficiency decreased both (II) and, to a greater extent, (I). In early leaves little difference in sugar contents appeared before external symptoms of deficiency. Consistent differences in (I) level occurred only after tillering. During senescence the (I) of the earliest leaves declined with advancing age. In later leaves the reverse change occurred at varying stages of growth. In K-deficient plants the decline in (I) with increasing age was general. The ratio sucrose/(II) was high in N-, low in K-, and intermediate in P-deficient plants. High vals. for (II) in P deficiency are related to the high ratio of amide-/NH_2-N, both vals. increasing rapidly at the emergence of the fourth leaf. Changes in (I) level are discussed in relation to C assimilation, translocation, protein synthesis, respiration, and meristematic activity. A. G. P.

Fixation and transfer of nitrogen in the soya bean with special reference to the mechanism of transfer of fixed nitrogen from bacillus to host. G. Bond (Ann. Bot., 1936, **50**, 559—578).—A large proportion (probably 80—90%) of the N fixed by nodule bacteria diffuses into the host cytoplasm and is translocated to other parts of the plant. Storage of N by the organisms is small. Fixation of N is regarded as a form of respiratory activity rather than a stage in the synthesis of bacterial protein. The decline in N-fixing activity with advancing growth of the plant may result from diminished supply of carbohydrate to the bacteria or to the accumulation of inactive organisms. A. G. P.

Fat oxidation system in *Lupinus albus*. F. N. Craig (J. Biol. Chem., 1936, **114**, 727—746).—Pulverised seeds of *L. albus*, when shaken with H_2O, consume O_2 and form CO_2 with a CO_2/O_2 ratio $\ngtr 0\cdot3$. There is a small anaërobic production of CO_2. The optimum $p_{\rm H}$ is approx. 7 in PO_4''' buffer, but no O_2 is used up below 4 in HCl–citrate or above 12 in NaOH–glycine buffers. Acid is produced in very small quantity during the reaction, which is due to a mixture of enzymes on the oil or fatty acid in the seed. O_2 consumption is inhibited by CO, urethane, and under certain conditions by KCN, but is increased by PO_4''' and sometimes by KCN. Vals. of μ in the Arrhenius equation are 11,700 between 5° and 35° when the system is saturated with oil, and 15,200 above 30°, and 3500 below 20° in absence of added oil. J. N. A.

Mechanism of symbiotic nitrogen fixation. I. Influence of nitrogen pressure. P. W. Wilson (J. Amer. Chem. Soc., 1936, **58**, 1256—1261).—The fixation of N_2 by red clover (*Trifolium pratense*) in absence or presence of A and He is independent of p_{N_2} $>0\cdot1$—$0\cdot2$ but decreases rapidly when $<0\cdot1$ atm. This function of p_{N_2} is characteristic of the N-fixing process; it is not observed in plants supplied with combined N. H. B.

Phæophytin formation in leaf organs after temperature effects. M. Röben and M. Stern (Kl. Mitt. Ver. Wasser-, Boden-, Lufthyg., 1935, **11**, 47—56; Chem. Zentr., 1935, ii, 2835).—Phaeophytin (I) cannot be detected spectroscopically in heated or frozen leaves, moist and dry heat and chilling showing the same effect, but depending on the reaction of the sap. Withered and dried leaves contain no (I). R. N. C.

Platinum-gold difference in relation to the potential of indifferent electrodes in tissue pulp of potato tubers. H. Wartenberg (Planta, 1935, **24**, 711—724).—In certain cases the initial stage of biological oxidation processes, viz., the transference of the oxidative power from O_2 to a reversible carrier, can be followed potentiometrically by utilising the difference in O_2 sensitivty of Pt and Au electrodes. The method is applied to the examination of tyrosinase activity in potato tuber by means of the O_2 consumption during melanin formation. A. G. P.

Delayed killing of maize seedlings with *X*-rays. G. N. Collins and L. R. Maxwell (Science, 1936, **83**, 375—376).—Irradiation of dried seeds with *X*-ray dosages within a certain range resulted in the death of all plants in the seedling stage without impairment of germination. Higher doses completely inhibited germination. A cytological explanation of these results is discussed. L. S. T.

Variations of the nitrogen content of the lily-of-the-valley during forcing. R. Quetel (Compt. rend., 1936, **202**, 2096—2098).—The changes in N content during forcing with Et_2O are similar to those of the lilac (A., 1933, 758). H. D.

Effect of acraldehyde on the structure of the plant cell. M. Mascré (Compt. rend., 1936, **202**, 2094—2096).—The modifications of the tissues of lupins, peas, and of *Allium* by exposure to acraldehyde vapour are described. H. D.

Isoelectric point of plant protoplasm. G. Yamaha (Sci. Rep. Tokyo Bunrika Daigaku, 1936, **2**, B, 209—221).—The isoelectric points (determined by cataphoresis and/or dye-fixation) of spermatia, zoospores, various parts of pollen mother cells, and of single algæ have vals. between p_H 3·0 and 4·5. F. O. H.

Chemical composition and structure of the plant plasma. H. Kaho (Keem. Teated, 1934, **2**, 17—26; Chem. Zentr., 1935, ii, 2968).—A review. The rôle of lipins as dispersive agents in the plasma is emphasised. A. G. P.

Concentration of solutes in [plant] sap and tissue and the determination of bound water. T. G. Mason and E. Phillis (Ann. Bot., 1936, **50**, 437—454).—Comparison of the sugar and Cl′ contents of expressed sap, of the press-residue and of whole leaves of cotton indicates the presence of bound H_2O in the tissue. The amount of sap-sol. K (and probably that of other constituents) cannot be determined by aq. extraction of oven-dried material. Approx. 25% of the total K in leaves is not dissolved in the sap. There is no evidence of absorption of sucrose or Cl′ by tissue. The concn. of these constituents in intact plants is best determined in sap expressed from frozen material. A. G. P.

Content and alkalinity of the ash of beetroot. H. Colin and M. Simon (Compt. rend., 1936, **202**, 2171—2173).—The ash content of the root, stem, and leaves of dried edible and sugar beet is approx. const. (11·0—14·0%) even when grown in soil containing varying amounts of N fertiliser. The acid val. of the ash varies, that of the edible beet being the higher. F. N. W.

Presence of maltose in the storage organs of *Lathyrus silvestris*. A. Meunier (J. Pharm. Chim., 1936, [viii], **24**, 9—17; cf. A., 1933, 990).—Maltose is isolated from the roots of *L. silvestris* by pptn. with $Ba(OH)_2$. The content in the roots falls to a min. in December. H. D.

Determination of small quantities of fermentable sugars [in plant materials] by carbon dioxide production. W. O. James and A. L. James (New Phytol., 1936, **35**, 1—10).—Determination of sugars by loss of reducing power after fermentation with yeast gave erroneous results in the case of barley embryos when the material was aërated to prevent formation of EtOH. Reducing substances (probably CHAcMe·OH) were formed during the fermentation. Better results are obtained by measurement of CO_2 evolved [$Ba(OH)_2$ method] during fermentation with a starved yeast culture in the presence of HCN and in an atm. of N_2. A separate determination is made of CO_2 evolved during autofermentation of yeast. Disaccharides are preferably hydrolysed and determined as hexose. A. G. P.

Soya-bean proteins. II. Preparation of glycinin. R. J. Hartman and L. T. Cheng (J. Chinese Chem. Soc., 1936, **4**, 152—156).—Improvements in Osborne and Campbell's method (A., 1898, ii, 626) are suggested. F. R. S.

Tryptophan and chlorophyll in the leaves of seedlings of barley mutants. N. Löfgren (Z. physiol. Chem., 1936, **241**, 142—147).—Tryptophan (I) is determined by heating the dried material with 20% aq. NaOH at 150° for 2·5 hr., adding H_2SO_4, pptg. with $HgSO_4$, dissolving the ppt. in HCl, and repptg. with the reagent of Folin *et al.* (A., 1927, 892) followed by photometric measurement. In the leaves of chlorophyll-defective barley mutants there is no relation between gramine (A., 1935, 1040) and (I) contents but the (I) levels are low compared with those of normal barley plants. The chlorophyll contents of various mutants appear to bear a simple relation to each other. W. McC.

Amino-acids of plants. I. Tryptophan content of leguminous plants at different stages of growth. A. I. Virtanen and T. Laine (Biochem. J., 1936, **30**, 1509—1513).—A method for determining the tryptophan (I) content of plants is described. With peas and clover, the content of (I) (as % of total N) is a max. at an early stage of growth before blooming, the level in the plants being double that in the seeds; the val. then falls rapidly until it is only slightly > that in the seeds. With peas there is a definite fall in the abs. amount of (I), but during the early stages of growth there is a remarkable rise, which possibly plays an important part in the metabolism of the young plant. The carotene and (I) contents of clover reach a max. simultaneously. J. N. A.

Non-protein-nitrogen of pulses. II. Partitioning of the nitrogen and determination of the essential amino-acids. K. Bhagvat and M. Sreenivasaya (Biochem. J., 1936, **30**, 1416—1418; cf. A., 1935, 672, 1936, 913).—A discrepancy between the Van Slyke and enzyme methods of arginine (I) determination in the seeds of *Phaseolus mungo* and *Cicer arietinium* indicates the presence of a new base other than (I). H. D.

Histochemical localisation of hordenine in barley plantules. R. Reilhes (Compt. rend. Soc. Biol., 1936, **122**, 852—854).—The alkaloid is localised, together with lipoid substances, in the young vacuoles of the meristematic cells. H. G. R.

***Strophanthus dichotomus*, D.C.** A. H. Millard (Pharm. J., 1936, **137**, 147—148).—The seeds yield a powerful cardiac poison on extraction with 70% EtOH. Extracts are distinguished from those of other varieties of *Strophanthus* by the colour reactions with H_2SO_4, resorcinol–HCl, and PhOH–HCl. F. O. H.

Alkaloid in *Vallesia dichotoma*. V. Cárcamo (Bol. Soc. Quim. Peru, 1936, **2**, 25—26).—A preliminary account of an alkaloid or alkaloids present in the "cuncuna," a plant indigenous to Peru. L. A. O'N.

Alkaloids of *Fritillaria roylei*.—See this vol., 1131.

Alkaloids of *Lupinus barbiger*.—See this vol., 1131.

Chemical composition of carob seed. G. Iglesias (Anal. Fís. Quím., 1935, **33**, 114—118).—The albumin of seeds of *Ceratonia siliqua* (cf. B., 1935, 779) from Majorca contains 77% of mannose and 23% of galactose (cf. Bourquelot *et al.*, A., 1899, i, 968). The embryo contains 6·51% of protein. The phytin, isolated by Boutwell's method (A., 1917, i, 374), contains 42·3% P_2O_5 and is free from inorg. phosphates. F. R. G.

***Cuscuta reflexa*, Roxb. III. Constituents of the seed-oil.** R. R. Agarwal and S. Dutt (J. Indian Chem. Soc., 1936, **13**, 264—267; cf. A., 1935, 1550).—The seeds contain 0·05% of cuscutalin, a flavone, and an oil, which yields linolenic (9·92), linoleic (17·26), oleic (25·58), stearic (27·2), and palmitic acid (11·5%), and 1·8% of unsaponifiable matter, including a *phytosterol*, m.p. 134—135°, $[\alpha]_D^{29}$ −30·9° in $CHCl_3$ (*acetate*, m.p. 124—125°). R. S. C.

Latex of *Brosimun galactodendron*. J. Gómez (Anal. Fís. Quím., 1935, **33**, 360—363).—The latex contains 3·48% of rubber, a cryst. wax, m.p. 64—65°, and α-amyrin. F. R. G.

Preparation and constitution of alginic acid.—See this vol., 1093.

Glycosides of madder.—See this vol., 1095.

Amolonin and its hydrolysis products.—See this vol., 1095.

Colouring matter of the flowers of *Lantana camera*, Linn. J. B. Lal (Proc. Nat. Acad. Sci. India, 1936, **6**, 128—130).—The flowers contain an anthocyanin and carotene. The former, isolated from the AcOH extract of flowers, yields reddish-purple *camerin hydrochloride*, m.p. 195° (sintering 180°). A. G. P.

Odorous substance containing sulphur from "shoyu." S. Akabori and T. Kaneko (Proc. Imp. Acad. Tokyo, 1936, **12**, 131).—The volatile part of "shoyu" contains OPr·SMe, isolated as the *compound*, $C_4H_{10}OS,2{\cdot}5HgCl_2$, m.p. 128—128·5°. J. N. A.

Resin of *Dacrydium Colensii*. Diterpene alcohol from *D. biforme* wood.—See this vol., 1115.

Hu-man-chiang. T. Okanishi (Japan. J. Med. Sci., IV, **7**, No. 1; Proc. Japan. Pharmacol. Soc., 1933, 62—63).—The toxic components of *Gelsemium elegans* are substantially the same as those recorded for *G. sempervirens*. Ch. Abs. (*p*)

Components of leaves of *Ficus carica*.—See this vol., 1121.

Organic nitrogen bases from pyrolysis of cotton-seed meal.—See this vol., 1123.

Determination of alcohol.—See this vol., 1091.

Determination of pentoses as furfuraldehyde in citrus fruits. W. B. Sinclair and E. T. Bartholomew (Amer. J. Bot., 1935, **22**, 829—842).—The bromate method gives practically theoretical results for furfuraldehyde (I) but the conversion of *d*-xylose and *l*-arabinose into (I) by the customary acid distillation method is incomplete. In the examination of citrus fruits the (I) distillate contains substances which interfere with the BrO_3', but not with the phloroglucinol method of analysis. Pre-extraction with 95% EtOH and Et_2O removes the interfering materials. Data for the peel of Valencia and navel oranges and of lemons are given. A. G. P.

Identification of lactose, alone or associated with glucose, in urine. F. Moreno Martín and A. Sebastián (Anal. Fís. Quím., 1935, **33**, 931—936).—Umikoff's reaction (warming with aq. NH_3 and NaOH) is proposed for the detection of lactose (I). 0·5 part per 1000 can be detected in 3 c.c. of urine whether glucose (II) is present or not. (I) is removed by warming with animal charcoal until no positive Umikoff reaction is given, (II) (or other sugars) in the filtrate being determined with Fehling's solution. F. R. G.

Direct micro-titration method for blood-sugar. B. F. Miller and D. D. Van Slyke (J. Biol. Chem., 1936, **114**, 583—595).—Sugar is determined in the Fujita–Iwatake blood filtrate (A., 1932, 75), after removal of Cd with $BaCO_3$, by addition of a large excess of $Fe(CN)_6'''$ (I) and direct titration of the reduced (I) with $Ce(SO_4)_2$ with setopaline-*C* as indicator. The vals. obtained agree well with the fermentable sugar vals. H. D.

Determination of saccharides.—See this vol., 1133.

Enzymic histochemistry. Micro-determination of alkalis in tissue. K. Linderstrøm-Lang (Compt. rend. Trav. Lab. Carlsberg, 1936, **21**, 111—122).—The tissue is ashed with a mixture of $Ba(OH)_2$, $BaCO_3$, and $BaCl_2$; the ash is extracted with H_2O and the extract, which contains NaCl, KCl, $BaCl_2$, and traces of $CaCl_2$ and $MgCl_2$, is treated with $(NH_4)_2CO_3$ and aq. NH_3 to remove Ba, Ca, and Mg. On evaporating the filtrate to dryness and igniting the residue only KCl and NaCl remain and are determined by electrometric titration of Cl′ (A., 1931, 1455). The method, applied to material containing $<4\times10^{-4}$ m.-equiv., is accurate to within 10^{-6} m.-equiv. W. O. K.